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May 20, 2003

Mr. Tien Q. Duong
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U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the second-quarter FY 2003 report for the Batteries for Advanced Transportation Technologies (BATT) Program, which contains summaries of the presentations to be given at the annual review of the BATT Program to be held May 28-29, 2003. This report and prior Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATT.html>.

Sincerely,

A handwritten signature in black ink that reads "Frank McLarnon".

Frank McLarnon
Manager
BATT Program

cc:	J. Barnes	DOE/OAAT
	R. Kirk	DOE/OAAT
	V. Battaglia	ANL
	K. Abbott	DOE-Oakland

LBID-2467

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) PROGRAM

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BATT PROGRAM OVERVIEW

Frank McLarnon
Lawrence Berkeley National Laboratory

The Batteries for Advanced Transportation Technologies (BATT) Program is supported by the U.S. Department of Energy Office of FreedomCAR and Vehicle Technologies to help develop high-performance rechargeable batteries for use in electric vehicles (EVs) and hybrid-electric vehicles (HEVs). The work is carried out by the Lawrence Berkeley National Laboratory and several other organizations, and is organized into six separate research tasks. The BATT Program addresses fundamental issues of chemistries and materials that face all lithium battery candidates for DOE EV and HEV applications. Emphasis is placed on the assembly of components into battery cells with determination of failure modes, coupled with strong efforts in materials synthesis and evaluation, advanced diagnostics, and improved electrochemical models. The selected battery chemistries are monitored continuously with periodic substitution of more-promising components.

During the past two years, the BATT Program has focused on three “baseline” cell chemistries: (i) a polymer-electrolyte cell with a Li metal anode, $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N} + \text{PEO}$ -based electrolyte, and a V_6O_{13} or a tunnel-structure Li_xMnO_2 cathode; (ii) a gel-electrolyte cell with a natural graphite anode, $\text{LiBF}_4 +$ cross-linked gel electrolyte, and a LiFePO_4 or sulfur-doped spinel cathode; and (iii) a Li-ion chemistry that is basically a high-energy version of the DOE Advanced Technology Development (ATD) Program “Generation 2” high-power cell with a graphite-based anode, $\text{LiPF}_6/\text{EC-EMC}$ electrolyte, and a $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$ -based cathode. The BATT Program is now in the process of redefining its baseline systems, and leading candidates are:

1. A high-energy cell with a $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode, $\text{LiPF}_6/\text{PC-EC-DMC}$ electrolyte, and a carbon-coated graphite anode. This can be regarded as the next generation of the existing $\text{LiNi}_{0.8}\text{Al}_{0.05}\text{Co}_{0.15}\text{O}_2$ in $\text{LiPF}_6/\text{EC-EMC}$ baseline system. It contains a cathode that is not only less expensive but can also provide higher energy. The lower-cost PC-containing electrolyte is possible due to an amorphous carbon coating that prevents anode exfoliation.

2. Continued work on the LiFePO_4 system, but focused on PC-EC-DMC instead of a gel electrolyte. It is believed that significantly improved materials can be developed through the use of a liquid electrolyte, without the complications of a gel. This could be regarded as a moderate-energy, low-voltage system that is inherently stable and low cost.

3. A high-rate liquid-electrolyte/spinel system paralleling work in the ATD Program to develop a low-cost high-power battery. This essentially replaces the sulfur-doped spinel system.

The six primary BATT Program task areas are: (1) Cell Development, (2) Anodes, (3) Electrolytes, (4) Cathodes, (5) Diagnostics, and (6) Modeling. Task 1 comprises cell fabrication, testing and characterization, Tasks 2-4 are aimed at identifying new materials, and Tasks 5-6 support all BATT Program work. The remainder of this report includes summaries of the presentations to be made by BATT Program Principal Investigators at the annual review meeting held May 28-29, 2003.

BATT TASK 1 CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-cost Li-ion and high-power Li-ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to benchmark the performance of new materials for low-cost and high-power Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell, and then tested using a consistent protocol to determine cell capacity, energy, power, and lifetime characteristics. Tested cell components are then delivered to appropriate investigators involved with BATT Program diagnostic projects. Fabrication of baseline polymer-electrolyte cells is carried out in BATT Program Task 3.2.

STATUS OCT. 1, 2002: The analysis of capacity and power fade mechanisms for Li-ion cells with Gen 2 materials was completed in coordination with the ATD Program. The initial benchmarking of the low-cost Li-ion cell with LiFePO_4 and natural graphite in liquid and gel electrolyte was completed.

EXPECTED STATUS SEPT. 30, 2003: Efforts on the low-cost Li-ion baseline cell will be focused on LiFePO_4 cathodes, various gel electrolyte components applied to Celgard separators, and the evaluation of the available natural graphites. Characterization of LiFePO_4 materials prepared *via* different synthetic processes will be compared. Electrode compositions will be optimized for electronic and ionic conductivity with the aid of collaborative modeling studies (J. Newman and A.M. Sastry). New materials for the base line cells will be evaluated including, doped LiFePO_4 , $\text{Li}(\text{Ni},\text{Mn})\text{O}_2$, $\text{Li}_{0.44}\text{MnO}_2$, and intermetallic anodes.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade.

MILESTONE: (a) Benchmark the performance of the $\text{LiFePO}_4(\text{UdM})/\text{natural graphite}$ cell with liquid electrolyte - December 2002. (b) Compare performance of LiFePO_4 from different sources - May 2003. (c) Evaluate cycle performance and power capability of the LiFePO_4 / gel polymer electrolyte / natural graphite cell - August 2003.

Development of the Natural Graphite / LiFePO₄ Cell

Kathryn A. Striebel
Lawrence Berkeley National Laboratory

The primary objective of the project is to benchmark the performance of new materials for low-cost and high-power Li-ion cells capable of meeting the USABC and FreedomCAR goals for energy density, power density, cost, and cycle life. In FY2003, the performance and failure modes of the low-cost baseline cell containing natural graphite and LiFePO₄ electrodes were studied and several avenues for improving the cycle life and power capability were investigated.

Early results on the testing of cells with both gel and liquid electrolytes revealed serious issues with capacity fade during 100% DOD cycling at C/2. In addition, the power capability of this cell was low, in large part due to the documented low conductivity of LiFePO₄. The mechanistic reasons for the capacity fade were addressed in a comparison of the performance of LiFePO₄/NG pouch cells with three different natural graphite anodes. Electrochemical diagnostics, carried out on electrode samples from disassembled cells, revealed that capacity fade was due to increases in the impedance of both electrodes, anode structural degradation, and a larger-than-expected loss of cyclable Li, mostly likely due to instability of the anode SEI. The different mechanisms varied with type of anode. Samples of these electrodes were supplied to the various diagnostics tasks. The degradation of the Mag-10 anode was often worse in pouch cells containing LiFePO₄ cathodes, as compared with those containing LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathodes (ATD Gen 2 high-power Li-ion cell chemistry), suggesting a negative influence of the LiFePO₄.

Several avenues for the improvement of the capacity retention of this cell were evaluated, including the addition of the additive vinylene carbonate (VC), the improvement of anode conductivity and the oxidative treatment of the natural graphite. The addition of the VC was successful in improving both the coulombic efficiency and the capacity retention with no apparent effect on the behavior of the LiFePO₄ cathode. The other approaches also appear promising, but they have not yet been completed.

The dependence of the impedance and high-rate utilization of the LiFePO₄ cathode on the nature and content of the conductive carbon added to the cathode was examined with a series of cathodes supplied by Hydro-Québec (K. Zaghib). With an optimal carbon content together with the use of a carbon-coated current collector (LBNL), the impedance of the cathode was lowered by an order of magnitude to values which bring it within reason for a high-power application. An analysis of the status of this cell in comparison with USABC and FreedomCAR goals will be discussed.

Finally, the high-rate utilization of several sources of LiFePO₄ were compared in a half-cell with a Li anode. At the highest rates (10C), the cathode supplied by MIT showed the best utilization. However, these cathodes were the thinnest of those tested, and a modeling effort is underway (V. Srinivasan, J. Newman) to facilitate comparisons of cathodes with different compositions and thicknesses.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

SYSTEMS: Low-cost, high-energy Li-ion

BARRIER: Short lithium battery lifetimes, inadequate capacity.

OBJECTIVES: Support cell development through structural characterization of active electrode components before, during, and after cycling. Investigate inexpensive, self-actuating overcharge protection mechanisms. Synthesize and evaluate alternative electrode materials.

APPROACH: Address primary causes of capacity and power fading by correlating them with changes in the composition and structure of electrode active materials. Techniques employed include x-ray diffraction (XRD), vibrational spectroscopy, and electroanalytical testing. Develop an internal overcharge protection mechanism based on an electrolyte or separator component that will internally short an overcharged cell. Discover improved cell systems through a limited program of synthesis and evaluation of alternative components.

STATUS OCT. 1, 2002: Phase transformations and accumulation of decomposition products (if any) in cycled electrodes from BATT Program Task 1.1 have been identified and correlated with cell performance characteristics. Efforts to assess the utility of electroactive polymers for overcharge protection in Li-ion batteries are ongoing. Some potentially useful new low-cost, high-capacity electrode materials have been prepared and evaluated.

EXPECTED STATUS SEPT. 30, 2003: Composition and structural analyses of BATT Program Task 1.1 electrodes will have contributed to our understanding of the failure and degradation modes in the baseline systems. The switching behavior of electroactive conducting polymers incorporated in Li-ion cells will have been characterized, and an assessment of their potential for providing overcharge protection will be underway. Additional new cathode materials will have been prepared and evaluated.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Construct and test an overcharge protection device utilizing an electroactive conducting polymer. (July 2003)

Cell Development Support, Overcharge Protection, Cathode Materials

Thomas J. Richardson
Lawrence Berkeley National Laboratory

This task addresses two important aspects of Li battery performance and safety. New low-cost, low-toxicity cathode materials with high capacity, good kinetics, and inherent stability are essential for meeting the goals of the DOE/FreedomCAR program. An inexpensive, effective overcharge protection system that does not compromise the energy and power density goals becomes increasingly indispensable as the use of large, high-voltage Li battery cell stacks in vehicles approaches reality.

Our approach to the development of new cathodes is to incorporate structures known to impart stability at high states of charge in iron, manganese, or other metal oxides with appropriate theoretical capacities. The redox stability and safety of the BATT baseline electrode LiFePO_4 (178 Ah/kg) led us to investigate phosphate-containing oxides such as $\text{Fe}_3\text{O}_3\text{PO}_4$, an iron (III) compound easily prepared by solid-state reaction in air, with a theoretical capacity of 259 Ah/kg. Another iron (III) phosphate, $\text{Fe}_{1.2}\text{PO}_4\text{X}$, where X is F, OH, or H_2O was synthesized by a hydrothermal method, and shows good cyclability in a single-phase system, $\text{Li}_y\text{Fe}_{1.2}\text{PO}_4\text{X}$, with x up to at least 1.

We have shown that electroactive polymers whose conductivity depends upon their state of charge can provide excellent overcharge protection in Li batteries. Using well-characterized thin films of these polymers, we are able to visualize the potential profile across a separator containing the polymer. This, in conjunction with a calculational model based on the conductivity vs. potential characteristics, demonstrates the ability of the polymer to adjust its conductance to the load applied. The result is a reversible, self-actuating, low-resistance internal shunt that allows overcharge currents to pass through a cell without damaging the components, maintaining the discharge capacity, and allowing the rest of the cell stack to operate normally.

TASK STATUS REPORT

PI, INSTITUTION: K. Zaghib, Hydro-Québec (IREQ)

TASK TITLE - PROJECT: Cell Development - Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIER: High cost of Li-ion batteries

OBJECTIVES: (a) To fabricate Li-ion polymer cells (4 cm² area) using cell chemistries proposed by DOE. Cells (50% of the total cells) will be sent to LBNL for testing. (b) To investigate interfacial phenomena at the anode/separator and cathode/separator in Li-ion polymer cells. (c) To determine the cycle life and self-discharge rates of Li-ion polymer cells at different temperatures (55°C to 0°C). (d) To synthesize low-cost graphite anodes and LiFePO₄ cathode materials for Li-ion polymer cells.

APPROACH: Our approach is to synthesize and coat electrodes (both anode and cathode) with low-cost materials, and use these materials to assemble prismatic cells. Additional work will be focused on gel polymers, as well as studies of pressure effects and interfacial phenomena at the polymer/electrode interfaces.

STATUS OCT. 1, 2002: Studies were completed on the effect of different amounts of conductive carbon (1% to 15%) on the performance of LiFePO₄ electrodes. The results indicated that 6% carbon added to LiFePO₄ provides a good compromise for energy and power, while still achieving a reversible capacity of 65% at 2C rate and 62% at 3C rate. The effect of solvent mixture and the type of Li salt on the performance of Li-ion polymer cells were determined. The electrochemical performance of a Hydro-Québec (HQ) solvent (TESA) mixed with EC (3/1) was comparable to GBL-EC (3/1). Thirty cells were provided to LBNL in FY 2002 for evaluation.

EXPECTED STATUS SEPT. 30, 2003: Coating of cathodes based on LiFePO₄ with different ratios of conductive carbon (from 3 wt% to 15 wt%) will be completed. The investigation of phenomena at the cathode/separator interface in Li-ion/polymer cells containing LiFePO₄ by *in situ* SEM will be ongoing. Analyses of the effects of carbon-coated LiFePO₄ cathode materials with different particle sizes on Li-ion polymer cell rate capability and cycle life will be ongoing. Fabrication of Li-ion/polymer cells (4 cm² area) using cell chemistries proposed by DOE will be complete, and 50% of the total cells will have been sent to LBNL for testing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10-year life, < 20% capacity fade.

MILESTONES: (a) Production of 60 Li-ion polymer cells (4 cm² area) by using highly viscous electrolyte based on GBL (γ -butyrolactone), TESA (tetraethylsulfamide), or mixed electrolytes will be completed by March 2003, with 50% of the total cells sent to LBNL. (b) Impedance and *in situ* SEM investigations of phenomena at the anode/separator and cathode/separator interfaces in Li-ion/polymer cells will be completed by May 2003. (c) Synthesis of low-cost carbon-coated LiFePO₄ cathode material for Li-ion/polymer cells will be completed by August 2003.

Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials

K. Zaghib

Hydro-Québec (IREQ), Varennes, QC, Canada

The successful commercialization of Li-ion gel polymer batteries for portable electronic devices has led to other applications where the thickness and weight of batteries are important. A considerable investment in this battery technology that utilizes LiCoO_2 cathodes has been made. However, lower-cost cathode materials are required for many applications such as in EVs and HEVs. Recently, LiFePO_4 was investigated intensively as a potential cathode material for rechargeable Li-ion batteries because of its low cost and safety.

In this presentation, we report the results obtained with natural spherical graphite/gel electrolyte/ LiFePO_4 cells. The mixed salts LiTFSI-LiBF_4 in EC-GBL solvent and the same molar concentration of the individual salts were used to study the salt effect. The effect of carbon additives in the cathode on cell performance was also investigated.

Thirty cells of, Li-ion (natural graphite/ LiFePO_4) and Li-metal (Li/LiFePO_4), were evaluated. These cells contained LiBF_4 , LiTFSI , or mixtures of these salts in EC/GBL (1:3). The Li/LiFePO_4 cells with 1-15% conductive carbon in LiFePO_4 electrodes were used to study the cathode performance. Charge-discharge cells were carried out using the galvanostatic method. AC impedance spectroscopy and *in situ* SEM were used to investigate the interface phenomena. The test cells were maintained at an optimum compression of 10 psi during the test. Both types of cells were evaluated at different rates between the voltage limits of 2.5V to 4V. A Bitrode cycler was used for long-term cycling tests.

Four samples of sphere-like natural graphite powders (3-D) with average particle size of 12, 20, 30 and 40 μm were obtained by a mechanical process, and were studied with gel electrolyte. The 20 μm particle seems to be a good compromise with capacity and coating process.

The salt effect was studied in Li-ion configuration by using EC-GBL (1:3) with LiBF_4 and LiTFSI salts. For the mixed salt (1M LiTFSI + 0.5 M LiBF_4 in EC/GBL), we find high capacity fade compared to the same molar concentration of the single salt LiTFSI .

The data show that increasing the carbon content in the iron phosphate cathode has a dramatic effect on high-rate performance. A 6% carbon content seems to be a good compromise with energy and power, with 65% of the reversible capacity at 2C-rate and 62% at 3C-rate. Even with 1% carbon, we obtain more than 50% of the reversible capacity at 3C-rate.

The cell $\text{LiFeO}_4/\text{Gel}/\text{NG}$ was cycled at 0 to 10°C between 2.5 V and 4 V, and the impedance was measured *in situ* before and after vacuum was applied. The impedance spectra showed no difference (before and after). The gel electrolyte was observed in the SEM chamber at different temperatures from -10 to 20°C and different pressure from 50 Pa to 100 Pa. Because no vapor pressure was detected from -10 to 10°C, we investigated the bowling and decomposition of gel electrolyte at 20°C and 100 Pa. A preliminary animation of all gel cells was established, and we will continue to develop this technique for this kind of technology.

BATT TASK 2

ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-cost Li-ion

BARRIER: Cost and safety limitations of Li-ion batteries

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our approach has been to search for and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above that of metallic Li, and capacities of 300 mAh/g and ~2000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The approach will be broadened in FY 2003 to include investigations of standard $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and electronically-conducting Li-, Mg-, and Al-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes against high-voltage layered and spinel cathodes. Such Li-ion cells, which should be inherently safe compared to conventional Li-ion cells, provide a voltage of ~3 V and may find application in high-power batteries for HEVs.

STATUS OCT. 1, 2002: We have identified several intermetallic compounds that react topotactically with Li, and by reversible Li insertion/metal extrusion processes. The major focus has been placed on $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$, Cu_2Sb and MnSb electrodes. Although these systems operate reversibly within strictly defined voltage limits, they still suffer from an unacceptably large irreversible capacity loss (ICL) on the initial cycle. Oxide surface layers, the choice of electrolyte, and the identity of the binder were determined to have a small effect on lowering the capacity loss, whereas the loss of extruded metal during the initial cycle and electronic isolation were determined to be major contributing factors in the loss of cell capacity. MnSb electrodes showed an ICL of 15-20% (similar to graphite electrodes) compared to $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$, Cu_2Sb and InSb electrodes (25-40%) and delivered a steady 300 mAh/g for 20 cycles.

EXPECTED STATUS SEPT. 30, 2003: We expect to increase the cycle life of intermetallic electrodes based on tin and antimony to more than 100 cycles with capacities in excess of 300 mAh/g (~2000 mAh/ml) in Li half-cells. We will have completed our initial investigations of standard $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li-, Mg-, and Al-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes that are coupled against high-voltage layered and spinel cathodes.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: (a) a reversible electrochemical capacity of tin- or antimony-based intermetallic electrodes in excess of 300 mAh/g (~2000 mAh/ml) for 100 cycles: September 2003.
(b) 100 cycles from ~3 V cells containing a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -type anode and a high-voltage layered or spinel cathode (September 2003).

Non-Carbonaceous Anodes

Michael M. Thackeray
Argonne National Laboratory

During FY2003, efforts were made to improve the electrochemical capacity and cycle life of Sn- and Sb-based intermetallic electrodes that operate by Li insertion/metal displacement reactions and to meet the performance goals of 300 mAh/g (~2000 mAh/ml) for 100 cycles. Although the capacity goal of 300 mAh/g could be achieved, the long-term cycling stability of the electrodes was strongly dependent on the voltage window selected for the electrochemical experiments. A study of Ag₃Sb electrodes demonstrated that the greatest stability could be obtained when the electrode was cycled between 0.7 and 0.0 V. In this instance, Li_xAg is cycled in a Li₃Sb matrix, which is analogous to the way in which a SnO_x electrode operates. The greatest limitation of intermetallic electrodes is still the irreversible capacity loss that occurs on the initial cycle, particularly when the electrodes are lithiated below 0.7 V vs. Li⁰. Diagnostic studies of cycled Cu₂Sb and Cu₆Sn₅ electrodes by X-ray Photoelectron Spectroscopy and Scanning/Transmission Electron Microscopy were undertaken to gather information about the SEI layer on the electrodes. Because of the severity of SEI formation that occurs during the reaction between lithiated intermetallic electrodes and organic-based electrolytes below 0.7 V, we plan to focus some of our future efforts on intermetallic negative electrodes that operate between 1.5 and 0.7 V vs. Li⁰. In addition, we have explored metal oxide anodes, such as modified Li₄Ti₅O₁₂ electrodes (coupled with 5 V spinel electrodes) and lithiated MgMoO₄, which operates at lower potential. These data will be discussed; strategies for future work will be presented.

(see cathode section later in this report)

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-cost Li-ion battery and gel-electrolyte battery

BARRIER: Cost, safety and volumetric capacity limitations of Li-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte. In particular, we will investigate Mn-tolerant anode materials.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2002: We have shown that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure Al was found to have a high capacity and react readily with Li, but its capacity faded rapidly upon cycling in carbonate-based electrolytes; Al-based alloys show behavior inferior to that of pure Al. Tin-containing materials, such as MnSn_2 , cycle well for a few cycles before capacity fade sets in. Pure Sn anodes appear to cycle better than MnSn_2 .

EXPECTED STATUS SEPT. 30, 2003: We expect to have designed a program to understand and remediate capacity fade upon cycling, and as a result to have identified several additional non-Al binary alloys, and to have improved the electrochemical performance of the materials identified.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) We will design a program to identify, understand, and mitigate the capacity loss upon cycling of simple alloy systems. This will result in a milestone to understand the cause of capacity fade in pure tin by June 2003, and to propose a means of remediating that fade.

(b) Another major milestone is to identify by September 2003 a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 V relative to pure Li.

Novel Anode and Cathode Materials

M. Stanley Whittingham
SUNY at Binghamton, Binghamton, NY

The goals of this project are to find improved transition metal oxide cathode materials for Li batteries and to gain a better understanding of what limits the use of simple alloys as the anode. In the cathode area major effort is being focused on stabilized layered manganese dioxides, and on building a base case cathode system using LiFePO_4 against which the manganese and other cathodes will be compared. In the anode area, the focus is being placed on tin materials, with the initial experiments being on pure tin foil.

Lithium Iron Phosphate. In 2002/2003 major emphasis was placed on understanding the behavior of lithium iron phosphate cathodes, a low cost cathode. The synthesis, stability and properties of this material were determined, and its electrochemical characteristics were measured for a number of different carbon coating processes. The initial resistance of these cathodes, synthesized from reagent grade chemicals, was around 10^6 ohm-cm. The capacity as a function of current density showed no major dependence on coating process when the total carbon level was above 6 wt%. Raising the temperature to 60°C increases the capacity to close to 100% - 170 mAh/g, at 1 mA/cm^2 . The substitution of part of the iron by manganese in LiFePO_4 reduced the overall capacity. Vanadium substitution in the Giniite form leads to a readily reversible $\epsilon\text{-LiVOPO}_4$.

Stabilized Layered Manganese Dioxides. The layered nickel/manganese system, $\text{LiNi}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$ has been studied for $0.33 \leq y \leq 0.5$ to determine the optimum composition, the nature of the electrochemically active specie, the role of cobalt, and to compare capabilities against LiFePO_4 . Physical and electrochemical characterization of these materials shows that they may best be described as stabilized nickel oxides. They are all significantly better electrical conductors than LiFePO_4 , and as we showed earlier for LiMnO_2 itself [1], the conductivity is enhanced by addition of cobalt. They show superior capacity performance relative to LiFePO_4 at all current densities. In addition, their higher discharge potentials and density leads to much higher gravimetric and volumetric energy densities.

Tin-Based Anodes. The presently used graphitic carbon anode used in Li cells has a relatively low capacity, and can pose safety problems under high charge rates. As a result a number of alloy forming metals have been studied. We are studying the behavior of bulk tin foil, where there is no need for conductive diluent or binder, and therefore minimum likelihood of side reactions. This allows a better understanding of what causes capacity fade in metal anodes. The electrochemical cycling of the tin foil has been compared with electrodeposited Sn and Sn_2Mn . The Sn foil shows equivalent or better behavior than the other electrodes. The Sn foil, even at cycling rates of 3 mA/cm^2 is comparable to Cu_6Sn_5 , formed *in situ* by heating a tin film electrodeposited on copper [2]. The phases formed, their grain size, and the cell impedance have been measured.

LiBOB Electrolyte. Our studies to date have used as electrolyte LiPF_6 in a mixed carbonate solvent. As the electrode cycling is strongly dependent on the electrolyte salt and solvent, we are studying the LiBOB salt in the same solvent mixture. We have synthesized the salt, and shown that it rapidly absorbs water to form a 1:1 hydrate, and forms solvates with most of the common solvents used in its purification and in battery use. In the EC/DMC mixed solvent, the Li is tetrahedrally coordinated by EC molecules. The layered manganates and tin itself have been cycled using LiBOB.

Collaborations and discussions have been held with Professors C. Grey (SUNY Stony Brook), G. Ceder (MIT) and A. Angell (Arizona State).

1. P. Sharma et al, *Elec. SS. Lett.* 1999; 2: 494; 2. N. Tamura et al, *J. Power Sources*, 2002, 107:48.

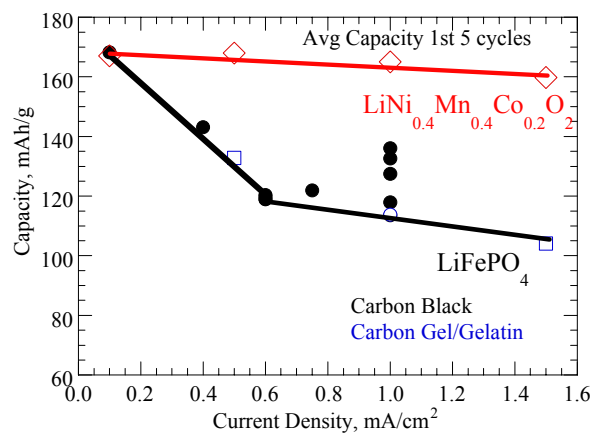


Figure 1. Capacity of LiFePO_4 and $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ cathodes (mean of first 5 cycles).

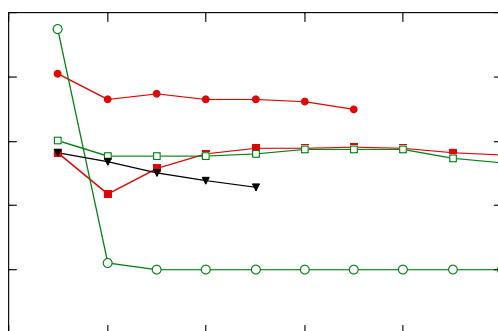


Figure 2. Cycling of tin foil compared to electrodeposited tin and in-situ formed Cu_6Sn_5 , and Sn_2Mn .

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and M.D. Curtis, University of Michigan
T. Malinski, Ohio University

TASK TITLE – PROJECT: Anodes - Novel Composite Anode for Lithium-ion Batteries

SYSTEMS: Low-cost Li-ion

BARRIER: Safety, irreversible capacity loss, and self-discharge

OBJECTIVES: Develop a low-cost and safe composite anode plate with no intrinsic irreversible capacity loss (ICL) and with higher gravimetric and volumetric energy density than the current carbonaceous anodes. Improve the kinetics of the Li insertion-extraction process in the composite anodes for application in high-power Li-ion cells.

APPROACH: Prepare composite anodes *via* reactive mechano-milling to eliminate large ICLs of metal-oxide anodes that occur during initial Li charge-discharge cycles. Form a desirable synthetic SEI layer *via* the mechano-reduction of oxide precursors and reduce the anode particle size to nanoscale to improve rate capability.

STATUS OCT. 1, 2002: The optimization of mechano-milling process parameters for reactive reduction of metal oxide anodes was in progress. The chemical nature of the SEI formed on metals and alloys after reduction of their oxide precursors was studied. An electrochemical study of the composite anode in baseline electrolyte (EC-DMC containing 1M LiPF₆) was ongoing. The process of developing composite anodes from mixed metal nitrides and oxides was in progress.

EXPECTED STATUS SEPT. 30, 2003: A well-controlled process based on reactive mechano-milling will be introduced for the preparation of composite anodes from various oxide or nitride precursors. Full characterization of the composite anodes in terms of their chemical composition, particle size, and nature of their SEI layer will be completed. Electrochemical tests of charge-discharge behavior of the composite anodes in terms of voltage profile, reversibility, and overall capacity will be completed. Cycle-life tests of the composite anodes at several levels of active material loading will be continued and accumulated cycle numbers and remaining capacity will be reported.

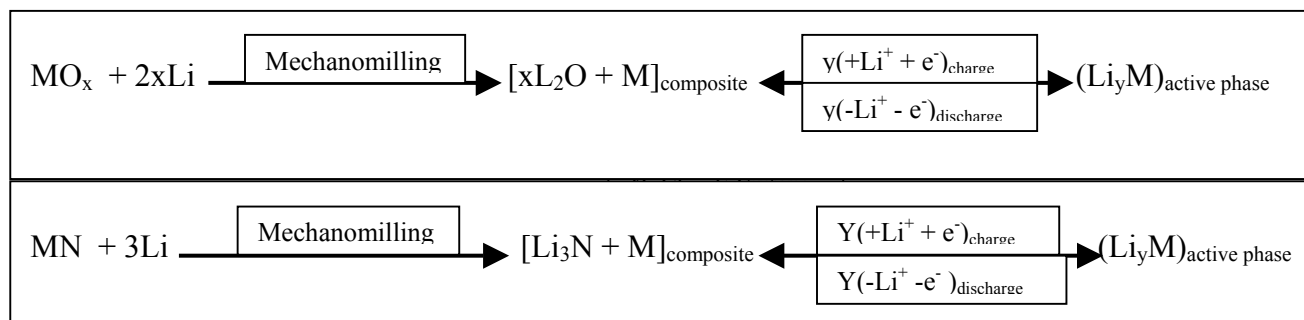
RELEVANT USABC GOALS: Exceeding 10-year life, low capacity loss (< 20%), good safety and high reliability (no toxic and flammable gas formation).

MILESTONES: (a) Optimization of process parameters for reactive mechano-milling of *sp* metal oxides completed by January 2003. (b) Electrochemical tests including charge-discharge cycle life of composite anodes formed by reactive milling of oxides and nitrides completed by August 2003.

Composite Anodes

Abbas Nazri¹, David Curtis¹ and Tadeusz Malinski²
¹ University of Michigan, and ² Ohio University

It is commonly observed that the first charge cycles of anodes and cathodes in Li-ion cells are different from their subsequent cycles. In some cases, it requires a few cycles to stabilize the anodes or the cathodes. Therefore construction of a balanced cell based on the initial capacity of electrode materials becomes more complicated. In addition during initial cycles, parasitic reactions occur which may reduce the cell cycle life, and may cause safety problems. This research work is based on a concept to stabilize the electrode materials before fabrication of electrode plates. The focus has been on the development of a process to stabilize composite anodes to provide a safer electrode with no irreversible capacity loss during initial cycles and no electrolyte decomposition. This process may simplify the engineering of balanced cells and battery modules. The process involves mechanomilling of anode materials (*i.e.*, oxides, nitrides, graphite, etc.) with Li or Li-containing precursors, according to the following formulations:



This process allows different degrees of lithiation of anode materials. The prelithiation can proceed to eliminate only the first cycle irreversibility or can exceed to include excess Li for stabilization of the cathode plate as well.

The large irreversible capacity loss of oxides and nitrides are eliminated by mechanomilling process when anode materials react with Li (chemically) to form a Li ion-conducting host (SEI-type overcoat). The nano-scaled metal phase is also formed during this milling process, and serves as an active anode phase during charge and discharge of the electrode. We have also synthesized bulk Li containing precursors chemically, such as LiC_6 , that reacts with oxides and nitrides favorably during mechanomilling process.

We have studied several oxides and nitrides using the mechanomilling prelithiation process. Anode plates were made from the above composites and tested in conventional but optimized multi-blend carbonate based electrolyte, (EC-DMC-PC, 50:30:20, containing 0.8M LiPF_6). We report our recent results for the electrochemical charge discharge cycles for the stabilized SnO , SnO_2 , Sb_2O_3 , CoO , CuO , Ge_3N_4 and Cu_3N . The results indicate that the lithium oxide coating provides a more protective film than the lithium nitride films. Although the gravimetric and volumetric energy density of oxides and nitrides based anodes exceed the capacity of LiC_6 , the >0.5 V, overvoltage hysteris between the charge and the discharge voltage profiles must be also considered.

BATT TASK 3 ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: N. Balsara, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Polymers for Li Metal Electrodes and Low-Cost Polymer Gel Cells

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities due to instability to 4 V.

OBJECTIVES:

- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (*e.g.*, 4 V) and develop materials and methods to increase stability.

APPROACH: To obtain a fundamental understanding of charge transport in polymers through polymer characterization and the synthesis of new materials. Polymers will be characterized by methods such as neutron scattering, dielectric relaxation spectroscopy, and light scattering to obtain new insights into the rate-limiting transport processes.

STATUS OCT. 1, 2002: New investigator.

EXPECTED STATUS SEPT. 30, 2003: The utility of neutron scattering, dielectric relaxation spectroscopy, light scattering, and rheological measurements will be fully explored for dry and gel polymers. A combination of polymer synthesis; physical, chemical, and electrochemical measurements; and theoretical calculations will be used to develop a working hypothesis on the limiting mechanism for Li-ion mobility.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

MILESTONE: Establish a working hypothesis for the rate-limiting step of Li-ion mobility in polymer electrolytes/polyelectrolytes (09/30/03).

Physical Characterization of Polymer Electrolytes

Nitash P. Balsara

Lawrence Berkeley National Laboratory/University of California, Berkeley

The rheo-dielectric properties of a low-M poly(ethylene oxide) (PEO; $M = 1000$) sample containing relatively concentrated lithium perchlorate (0.1 and/or 0.2 Li atom per EO monomer), were studied in the quiescent state as well as under steady shear. In the quiescent state, this PEO/Li system exhibited prominent dielectric dispersion attributable to the electrode polarization of Li cations. These cations were not freely moving in the matrix of PEO chains but were dynamically bound to the chains (at the oxygen in the monomer unit) to form a transient network of the chains. This was confirmed by rheological measurements that indicated that the zero-shear viscosity of the PEO/Li system was orders of magnitude larger than the viscosity of neat PEO. Under fast steady shear, the electrode polarization was even more enhanced. This enhancement was attributable to shear induced release of the Li cations from the PEO chains and the resulting rupture of the transient (dynamic) network of these chains. Correspondingly, the system exhibited shear-thinning of its steady flow viscosity in a range of shear rate where the electrode polarization was enhanced. The magnitude of thinning was close to the magnitude of the enhancement of the electrode polarization (within a factor of 2-3). This result suggested that the thinning corresponds to an acceleration of the chain motion resulting from the release of the Li cations (that dynamically bind/crosslink the chains in the quiescent state). Our experiments indicate that the longest relaxation time in the PEO/Li mixtures is of order 100 s. This is several orders of magnitude larger than that estimated from other techniques such as quasi-elastic neutron scattering [Mao et al, *Nature*, p. 163, v. 405, 2000].

The results described above were possible due to the availability of a unique rheo-dielectric apparatus for probing the fundamental dynamical properties of polymer electrolytes and gel systems. The apparatus consists of a conventional ARES rheometer with a specially machined cone-and-plate fixture that allows the application of electric fields and the measurement of dielectric properties. The cone and plate are connected to a frequency analyzer through a dielectric interface.

The limitations of PEO as a polymer electrolyte in Li ion batteries are well-established. In an attempt to combine the positive attributes of PEO and overcome the limitations, we have embarked on a program of studying nanostructured polymer electrolytes obtained from poly(ethylene oxide)-polyisoprene (PEO-PI) block copolymers. We have successfully synthesized our first PEO-PI block copolymer sample and are in the process of testing its promise as an electrolyte.

We continue to collaborate with the Kerr group on rheological and structural characterization of polymer electrolyte systems that they are studying.

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short Li battery lifetimes, poor ambient temperature performance for polymer electrolytes and low energy and power densities due to instability to 4 V.

OBJECTIVES: Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth. Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop materials capable of ambient temperature operation with Li metal. Determine the limits of stability of organic electrolytes at high-voltage cathode materials (e.g., 4 V) and develop materials and methods to increase stability.

APPROACH: A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

STATUS OCT. 1, 2002: Best polymer electrolyte transport and mechanical properties completed for TMO-containing comb polymers/LiTFSI or LiBETI (85°C: $t_+^0=0.3$, $D_s > 5 \times 10^{-12} \text{ m}^2/\text{s}$, $\sigma = 10^{-3} \text{ S/cm}$; 25°C: $t_+^0=0.2$, $D_s > 10^{-12} \text{ m}^2/\text{s}$, $\sigma \sim 10^{-4} \text{ S/cm}$, $E_g(\text{compression}) > 10^6 \text{ Pa}$). Less-costly salts (LiTf, LiPF₆ and LiBF₄) will also be measured and the cost vs. performance will be assessed. Dendrite-free cycling for > 500 coulombs in full cells at 0.2 mA/cm² [Lab cell (4cm²)]. Lithium/polymer cell testing at a larger cell size (e.g., 12.5 or 25cm² area) will be established

EXPECTED STATUS SEPT. 30, 2003: Effects of filler particles and cross-linking on transport and mechanical properties will be quantified for polymer electrolytes, polyelectrolytes, and polymer gels. Full and half-cell cycling and calendar tests will be used to quantify chemical side reactions and physical changes that limit battery life.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

MILESTONE: Demonstrate dendrite-free cycling of Li metal electrodes in full cells (Li/V₆O₁₃) and half-cells (Li/Li) for >1000 coulombs of charge (USABC goal >8,000 coulombs) at >0.5 mA/cm² with cell polarizations of <200mV(full cell) and <50mV(half-cell) at ≤60°C (09/30/03).

Polymer Electrolyte Research

John Kerr
Lawrence Berkeley National Laboratory

The behavior of polymer electrolytes at interfaces has been the focus of attention in the past year. Inhibition of polymer segmental motion by the presence of immobile surfaces is well known and gives rise to transport properties at surfaces that differ from the bulk. These interfacial effects play a significant role in several critical phenomena that determine the utility of Li batteries, such as dendrite growth, capacity fading and transport in composite electrodes, power capability and energy density. The behavior of old and new polymer electrolyte structures will be described in the context of these considerations. The salt anions have also been varied to provide changes in ion-pair strength and to search for less costly salts that may provide adequate performance. The effect of water contamination on polymer electrolyte performance has been assessed in order to determine the need for dry-box or dry room conditions for cell assembly.

Composite Electrolytes.

Extensive studies of the effects of added ceramic nanoparticle filler material (silica, alumina and carbon black) on the transport and mechanical properties of composite electrolytes has shown that the fillers reduce the conductivity and diffusion coefficient while increasing the mechanical moduli. The behavior is consistent with restriction of the segmental motion of the polymer by the filler and the magnitude of the effects depend on the nature of the polymer-particle interaction. Exposure of the composites to atmosphere results in increases in conductivity which strongly suggests that the improvements claimed in the literature for composite electrolytes are due to adventitious water bound to the filler particles. It was also noted that the presence of fillers appeared to affect the transport properties more than cross-linking of the polymers. These effects are also observed in polymer gels.

Composite Cathode Behavior for Polymer Electrolytes.

Since most formulations of composite cathodes contain a significant portion of carbon or acetylene black for electronic conduction purposes, the surface effects observed with composite electrolytes play a role in determining the behavior of the cathode. The concentration gradients generated within the electrodes will affect material utilization particularly at high rates. The effect of polymer structure and cathode formulation has been studied with the aid of reference electrodes, impedance spectroscopy and polarization experiments.

Dendrite Growth

The interfacial effects noted above appear to play a role in the initiation and growth of dendrites at Li metal electrodes. Experiments are continuing with the collaboration of the modeling group to determine the factors that control dendrite growth. Transport and mechanical properties are shown to be important and the effect of concentration gradients at both electrodes also appears to be important. The interfacial impedances appear to influence the rate of dendrite initiation.

New Polymer Structures for Improved Performance.

Progress on the synthesis and characterization of new polymer electrolytes that contain trimethylene oxide solvation units will be described. These materials show potential for improvements in both bulk and surface transport properties due to their increased flexibility.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University;
G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer

BARRIER: Short lithium battery lifetimes and high costs

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline and candidate systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data collected include elastic and viscous moduli, ionic conductivity, transference number, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2002: We have established that fumed silica-based composite electrolytes with low-molecular weight (MW) PEOs exhibit conductivities exceeding 10^{-3} S/cm at 25°C and have electrochemical properties decoupled from mechanical properties. We have determined that fumed silica stabilizes the Li/electrolyte interface, and effectively suppresses Li dendrite growth. We have found that addition of fumed silicas into low-molecular weight PEOs significantly improves charge-discharge cycle performance, coulombic and energy efficiencies, rate capabilities, and self-discharge performance of Li/V₆O₁₃ cells. We have determined that adding fumed silica improves the rheological properties of high-MW polymer electrolytes, but can be either beneficial or detrimental to ion-transport behavior. We have also found that adding fumed silica improves the interfacial stability of Li/electrolyte (high-MW PEO) interface and cycle performance of Li/V₆O₁₃ cells.

EXPECTED STATUS SEPT. 30, 2003: Using mixed-MW (high- + low-MW) PEOs + LiTFSI as the base electrolyte, we expect to determine the effect of fumed silica on conductivity and electrolyte/Li interfacial stability and how these results vary with type of fumed silica surface group.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) Interfacial stability and full-cell cycle studies of mixed polymer system completed by September 2003. (b) Rheological data for mixed-MW polymer system acquired for correlation with electrochemical stability by September 2003

Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

S.A. Khan, P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

The electrochemical and rheological properties of composite electrolytes comprised of surface-modified fumed silica nanoparticles + mixed-molecular weight (Mw) polyethylene oxides (PEO) + lithium salt (LiTFSI) were evaluated. Blends of PEO (Mw = 600,000) with polyethylene glycol-dimethyl ether PEG-dm (Mw = 250) in a 1:1 mass ratio were mixed with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) at 20:1 or 10:1 O:Li mol ratio. Two types of silica nanoparticles containing hydrophobic octyl groups (R805) or hydrophilic hydroxyl groups (A200) were evaluated. The ionic conductivity of the composite electrolyte is a function of both the salt content and temperature. Conductivity for the mixed-Mw PEO:LiTFSI (10:1) decreases from 15 to 90°C with addition of A200 or R805, whereas that for the mixed-Mw PEO:LiTFSI (20:1) increases from 15 to 30°C with addition of the fumed silicas but decreases above 30°C. We have measured the transference number of mixed-Mw PEO:LiTFSI (20:1) electrolytes at 23 and 65°C. The transference number increases with temperature but addition of fumed silica has a negligible effect. The interfacial stability of Li/mixed-Mw PEO electrolytes was assessed through open-circuit impedance at 65°C. All mixed-Mw PEO electrolytes have stable interfaces with Li compared to PEG-dm electrolytes (Mw = 250 and 500). Adding fumed silica improves the interfacial stability of Li/mixed-MW polymer electrolyte at high-current cycling. Li/electrolyte/Li cells using the mixed-Mw PEO systems were cycled at a current density of 1 mA/cm² and fixed charge density of 240 mC/cm². The average half-cell voltage without fumed silica increases considerably while the average voltage with fumed silica remains approximately constant, which is similar to the behavior observed in the low-MW PEG-dm system.

We also investigated the effect of fumed silica on Li dendrite inhibition and Al corrosion in PEGdm(250) + LiTFSI (1:20) electrolytes. *In situ* optical microscope observations and chronopotentiograms demonstrate that fumed silica suppresses Li dendrite formation. Linear sweep voltammetry and impedance measurements suggest that fumed silica may attenuate Al corrosion.

The dynamic rheological properties of mixed-Mw PEO with and without silica were characterized from 25 to 80°C. Additionally, the effect of LiTFSI was evaluated. Addition of LiTFSI plasticizes the mixed-MW PEO blend and reduces its viscoelastic characteristics. In contrast, the presence of fumed silica in the salt-containing blend produces a higher elastic modulus than that in a blend with no salt added. Furthermore, the mixed-Mw PEO electrolytes with fumed silica exhibit solid-like characteristics at all temperature, even above the melting point of PEO 600K. The surface groups on the silica nanoparticles, however, have different effects on the rheological properties: A200 produces a higher modulus than R805. These results, together with other studies, allows us to suggest that fumed silica nanoparticles increase the mechanical stability of the mixed-Mw PEO electrolytes by either networking directly or through bridging mechanisms with the polymer chain.

In summary, adding fumed silica nanoparticles improves the rheological properties of mixed-Mw PEO electrolytes and has a negligible effect on ionic transport properties. The mixed-MW PEO electrolytes have higher conductivities than the high-Mw PEO electrolytes and higher modulus than low-Mw polymer electrolytes; cells using these electrolytes do not need an additional separator.

TASK STATUS REPORT

PI, INSTITUTION: D. DesMarteau and S. Creager, Clemson University

TASK TITLE - PROJECT: Electrolytes - New Battery Electrolytes based on Oligomeric Lithium bis((perfluoroalkyl)sulfonyl)imide Salts

SYSTEMS: Li/polymer

BARRIER: Poor electrolyte transport properties, low power density, short lifetime

OBJECTIVES: (1) Develop methods for synthesizing oligomeric ionene Li salts based on the bis((perfluoroalkyl)-sulfonyl)imide anion. (2) Develop methods for preparing solid polymer electrolytes (SPEs) from the target salts. (3) Provide data on transport properties, especially ionic conductivity and Li ion transference, for target SPEs at variable temperature and composition.

APPROACH: Salts will be synthesized using methodologies developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem.* 1995, **72**, 203-208). SPEs will be prepared from crosslinked low-MW polyethylene glycol (PEG) and also non-crosslinked PEG for comparison. Transport properties will be measured using electrochemical impedance spectroscopy combined with other electrochemical techniques including restricted diffusion, DC polarization, and concentration cell techniques.

STATUS OCT. 1, 2002: A series of dimeric Li salts with different perfluorinated chains linking sulfonyl imide anions together, and selected oligomeric ionene salts utilizing perfluoroalkyl linkers in longer chains, were synthesized. SPEs from the salts will be fabricated in polyether matrices, and their ionic conductivities measured at various temperatures and compositions.

EXPECTED STATUS SEPT. 30, 2003: Synthetic methods will be refined for tetra-anionic imide Li salts with a range of different perfluoroalkylene chains linking imide groups, and for oligomeric imides. Ionic conductivities will be measured for SPEs made using all new salts. For salts that exhibit especially favorable behavior a more complete set of transport data including transference and salt diffusion measurements will be made, initially in collaboration with other BATT Program participants and later at Clemson. Salts that exhibit especially favorable properties will also be synthesized in larger quantities and made available to other BATT Program participants for further testing.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade, specific power 300 W/kg.

MILESTONE: (a) Prepare oligomeric Li salts of the type $\text{CF}_3\text{SO}_2[\text{N}(\text{Li})\text{SO}_2\text{R}_f\text{SO}_2]_n\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ with variable fluorocarbon linkers and systematic variation of the average n values. Refine synthetic methodology to improve yields, purity, and ease of the multi-step syntheses. (b) Perform a full transport properties study including measurement of conductivity and Li transference across a range of salt concentrations for a representative oligomeric imide salt. Milestones to be completed by September 2003.

Battery Electrolytes Based on Oligomeric Lithium bis((perfluoroalkyl)sulfonyl)imide Salts

Darryl DesMarteau and Stephen Creager, Department of Chemistry, Clemson University

Progress in the June 2002 - May 2003 time period was realized in both synthesis and characterization of new bis[(perfluoroalkyl)sulfonyl]imide Li salts for high-conductivity, high-Li-transference battery electrolytes. In the area of synthesis, all members of the ionene series of structure $\text{CF}_3\text{SO}_2\text{N}(\text{Li})[\text{SO}_2(\text{CF}_2)_x\text{SO}_2\text{N}(\text{Li})]_n\text{SO}_2\text{CF}_3$ with $x=4,6$ and $n=0,1,3,5$, and 17 have now been synthesized using a stoichiometric step-growth polymerization method developed at Clemson. Solid polymer electrolytes (SPEs) were made in polyether hosts using nearly all of these salts, and ionic conductivities were measured at different salt loadings and temperatures. In addition, a new allyl-ether-based lithium sulfonate monomer of structure $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CF}_2\text{CFH}-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_3(\text{Li})$ was synthesized from allyl alcohol and a commercially available material of structure $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$. The allyl ether salt is targeted for use in preparing single-ion conductors from hydrosilyl-terminated polyether comb polymer being developed by Kerr, a BATT participant at LBNL. Work in progress is aimed at preparing a material of structure $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CF}_2\text{CFH}-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$, which should behave similarly except for having greater Li salt dissociation and therefore higher ionic conductivity.

Measurement activities focused on composite SPEs incorporating inorganic oxides in polyether-based SPE formulations, and on restricted-diffusion measurements of salt diffusion in polyether-based SPEs. In the first area, SPEs were fabricated from low- and high-MW PEO using monomeric ($n=0$), dimeric ($n=1$), and hexameric ($n=5$) imide Li from the ionene series, with and without addition of silica, SiO_2 A300, specific surface area $300 \text{ m}^2/\text{g}$. This work follows that of Khan in the BATT program, extending it to the imide salts being studied at Clemson. Conductivities were not substantially affected by the silica when the high-MW PEO was used as host, however for low-MW PEO host the silica-containing SPEs had slightly higher conductivity. Restricted diffusion measurements utilizing a combination of galvanostatic polarization at different current densities with current-interrupt potential relaxation were used to obtain salt diffusion coefficients for a series of oligomeric salts with $x=4$ and $n=0,1,5,17$, and 225. For LiTFSI (monomer, $n=0$) in PEO host at a Li:EO ratio of 1:30, we measured a diffusion coefficient of $5.5 \times 10^{-8} \text{ cm}^2/\text{s}$ at 90°C , in close agreement with the value of $5 \times 10^{-8} \text{ cm}^2/\text{s}$ at 85°C reported by Doeff and co-workers from LBNL. Similar methods were used to obtain salt diffusion coefficients of $2.1 \times 10^{-8} \text{ cm}^2/\text{s}$ for the dimer ($n=1$), $1.1 \times 10^{-8} \text{ cm}^2/\text{s}$ for the hexamer ($n=5$), and $5 \times 10^{-9} \text{ cm}^2/\text{s}$ for the octadecamer ($n=17$). The systematic diminution of diffusion coefficient with increasing anion chain length is consistent with the expectation that the anion contribution to ionic transport will be diminished as the anions become larger. These measurements will be used together with concentration-cell measurements to be made in collaboration with BATT scientists at LBNL (Doeff and Kerr) to calculate Li-ion transference numbers for each SPE. Other project activities still in progress include studies at Clemson of ionic conductivity in EC/PC/PAN/imide salt gels, studies in collaboration with Steve Greenbaum at CUNY using solid-state NMR to measure individual ion self-diffusion coefficients, and calculations in collaboration with Hansong Cheng from Air Products of the atomic charge distributions in gas-phase and solvated monomeric and dimeric lithium imide salts.

TASK STATUS REPORT

PI, INSTITUTION: G.D. Smith and O. Borodin, University of Utah

TASK TITLE - PROJECT: Electrolytes - A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Lithium Cations in Polyether-based Solid Polymer Electrolytes

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Poor cation transport properties in solid polymer electrolytes

OBJECTIVES: Study the influence of polymer structure on ion complexation, dynamics and transport properties of polyether-based polymer electrolytes. Estimate the success of various strategies for the design of solid polymer electrolytes with improved transport properties.

APPROACH: Employ ab initio quantum-chemistry calculations to obtain energetics of polyether complexes with Li-salts and use these data to develop classical force fields for polyether/LiBF₄. Extend these studies to single-ion conductors and gel electrolytes. Use atomistic molecular dynamics simulations of polyether-based Li polymer electrolytes for parametric investigation of the influence of polyether structure, strength of the polyether-Li and Li-anion interactions and barrier of conformational isomerization reaction on ion transport.

STATUS OCT. 1, 2002: Force fields for poly(ethylene oxide)/LiBF₄, poly(oxymethylene)/LiBF₄, poly(propylene oxide)/LiBF₄, and poly(trimethylene oxide)/LiBF₄ were developed. Molecular dynamics simulations of these linear polyethers were performed.

EXPECTED STATUS SEPT. 30, 2003: A force field for the poly(ethylene oxide-trimethylene oxide) (EO-TMO) alternating copolymer doped with LiBF₄ will be developed. Molecular dynamics simulations of linear polyether-based polymer electrolytes will be completed, including EO-TMO. Parametric studies of the influence of PEO-Li⁺ interaction of structural and dynamic properties will be completed. A force field for comb-branch copolymers with polyether side chains will be developed and validated. The mechanism of ion transport in comb-branch copolymers with polyether side chains will be determined. Molecular modeling of gel electrolytes and single ion conductors will be initiated. MD simulations will be performed on liquid electrolytes (EC/LiTFSI) and initiated for comb-branched PEO based gels with EC plasticizer and TFSI⁻ anion attached to side-chains.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade.

MILESTONE: (a) Complete studies of linear polyether-based polymer electrolytes doped with LiBF₄ and parametric studies of the influence of PEO-Li⁺ interaction of structural and dynamic properties (February 2003)
(b) Develop quantum chemistry based force field for ethers/LiTFSI perform analysis of ion transport in comb-branch copolymers with polyether side chains (July 2003)
(c) Initiate MD simulations of PEO-based single ion conductors and gel electrolytes (September 30, 2003).

Molecular Modeling of Solid Polymer Electrolytes, Single Ion Conductors and Gel Electrolytes

Grant D. Smith and Oleg Borodin
University of Utah

Development of environmentally friendly and efficient electric vehicles (EV) and hybrid-electric vehicles (HEV) necessitates usage of high-performance rechargeable batteries. Lithium solid polymer electrolyte (SPE) technology is a potential candidate for use in EV and HEV applications due to ease of processing, good interfacial contact, mechanical stability and safety. Despite significant improvement of transport properties of SPE's over the last two decades, ionic conductivity and transference numbers of the currently available SPE's are still too low to design commercially viable Li batteries.

Linear unentangled SPE's comprised of polyethers doped with LiBF_4 have been investigated by molecular dynamics (MD) simulations at 393 K. Analysis of simulation trajectories indicated that the Li^+ motion along PEO chains yielded significant contribution to cation transport. Parametric investigations of the effect of barriers for conformational transitions and the strength of the Li^+ -polymer interactions on SPE's structure and transport properties have also been performed. Decrease of the barriers for polymer conformational transitions always facilitated polymer relaxation leading to enhanced ion transport, while changes of the Li^+ -polymer interactions could lead to either enhanced or diminished ion transport depending on the strength of the Li^+ /anion interactions. For SPE's such as PEO/ LiBF_4 at 393 K, exhibiting significant ion aggregation, a decrease of the Li^+ -polymer interactions resulted in the extensive ion aggregation and diminished conductivity. For the SPE's with a much lower Li^+ /anion binding energy than seen for $\text{Li}^+/\text{BF}_4^-$ the reverse tendency has been observed, namely, a decrease of the Li^+ /polymer interactions enhanced the Li^+ cation transport along PEO resulting in improved ionic transport.

Five polymers have been investigated as potential hosts for SPE's: poly(ethylene oxide) (PEO), poly(oxymethylene) (POM), poly(propylene oxide) (PPO), poly(trimethylene oxide) (PTMO), and a copolymer of poly(ethylene oxide – trimethylene oxide) (PEO-TMO). Quantum chemistry based force fields have been developed for all these polymers and their interactions with LiBF_4 . MD simulations of these polymers doped with LiBF_4 were performed at EO:Li=15:1, 393 K. POM melts had the slowest dynamics and lowest binding energies resulting in LiBF_4 salting out from POM/ LiBF_4 SPE's. The fractions of the uncomplexed or "free" Li^+ were predicted in the following order: PEO-TMO/ LiBF_4 > PEO/ LiBF_4 > PTMO/ LiBF_4 > PPO/ LiBF_4 , while polymer dynamics was predicted in the order: PEO \approx PEO-TMO \approx PEO \approx PTMO > PPO. In accord with the parametric studies, the ionic conductivities were predicted in the order: PEO-TMO/ LiBF_4 > PEO/ LiBF_4 > PTMO/ LiBF_4 > PPO/ LiBF_4 , with the difference between PEO-TMO/ LiBF_4 and PTMO/ LiBF_4 being similar to the simulation error bars for conductivity, *i.e.*, a factor of two. We conclude that the investigated structural changes of linear polyethers doped with LiBF_4 do not result in a significant improvement of SPE's transport properties suggesting that alternative strategies for design of novel SPE's be investigated.

Quantum chemistry based force fields have been developed for $\text{Li}^+/\text{TFSI}^-$, TFSI^- /ethers, as well as the poly(epoxide ether) (PEPE) comb-branch polymer. MD simulations of the PEPE/ LiTFSI at 393 K, EO:Li=15:1 have been initiated. Analysis of these systems will complement experimental information obtained by John Kerr's group and will aid in gaining a fundamental understanding of cation transport mechanisms and limiting factors for cation transport in comb-branched polymers. The quantum chemistry based force field for comb-branch PEPE-based single ion conductors with the TFSI anions attached to side chains is under development. MD simulations of the unplasticized single-ion conductors and single-ion conductors plasticized with EC, a gel electrolyte, are planned for the second half of the year.

BATT TASK 4 CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Low-cost (Li-ion) battery

BARRIER: Cost and safety limitations of Li-ion batteries

OBJECTIVES: To develop low-cost manganese oxide cathodes to replace LiCoO₂.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes for Li-ion cells. We will continue to focus on composite layered lithium-manganese oxide structures that are represented by the general formula $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ in which $\text{M}' = \text{Mn, Ti, Zr, Ru}$ and $\text{M} = \text{Li, Mn, Ni, Co}$ are showing excellent promise to replace LiCoO₂ as the cathode material of choice in Li-ion cells. In conjunction with our anode project, we will explore the electrochemical properties of high-potential layered and spinel electrodes against Li₄Ti₅O₁₂ and substituted, electronically-conducting Li₄Ti₅O₁₂ anodes in 3 V Li-ion cells that should be inherently safe.

STATUS OCT. 1, 2002: Preliminary investigations of $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ composite electrodes in which a Li₂M'O₃ component ($\text{M} = \text{Mn, Ti, Zr}$) was used to stabilize layered LiMO₂ electrode structures, particularly LiMn_{0.5}Ni_{0.5}O₂, were undertaken. These electrodes tend to show a relatively large irreversible capacity loss (ICL) during the initial cycles, but thereafter cycle with good electrochemical reversibility, and provide a rechargeable capacity of approximately 140 mAh/g between 4.6 and 2.5 V at room temperature and 160-170 mAh/g at 50 °C. These electrodes can accommodate extra Li to form Li₂MO₂ compounds with remarkable reversibility and without destroying the integrity of the layered structure; this finding has implications for using the surplus Li in Li₂MO₂ structures to combat the ICL at graphite and intermetallic negative electrodes.

EXPECTED STATUS SEPT. 30, 2003: Improvements in the electrochemical performance of $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ electrodes will have been achieved; the targeted performance goal is 190 mAh/g for 100 cycles at 50°C in Li-ion cells. The feasibility of using overdischarged electrodes (with Li₂MO₂ structures) as a reservoir for Li to combat ICL effects in Li-ion cells will have been determined. Composite $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ electrodes and spinel electrodes will have been evaluated against Li₄Ti₅O₁₂ and substituted Li₄Ti₅O₁₂ electrodes in ~3 V cells.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: (a) Evaluate $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ composite electrodes against a technical target of 190 mAh/g for 100 cycles at 50°C, and determine the feasibility of using overdischarged electrodes as a reservoir for Li; and (b) evaluate the electrochemical properties of composite $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ and spinel electrodes against modified Li₄Ti₅O₁₂ electrodes. (September 2003)

Novel Cathodes

Michael M. Thackeray
Argonne National Laboratory

We have aggressively pursued our approach to develop high capacity $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ “composite” electrodes ($\text{M}'=\text{Ti, Mn}$; $\text{M}=\text{Mn, Ni}$) with the goal of achieving 190 mAh/g for 100 cycles. NMR experiments, conducted in collaboration with C. Grey (SUNY, Stony Brook), confirm that these $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ structures are domain-like in character. Very high reversible capacities (~ 300 mAh/g) can be achieved from these electrodes if discharged from 4.6 V to low potentials (1.5 – 1.0 V); their reversible capacity, which is composition dependent, can exceed 200 mAh/g over the high-voltage range (4.6 to 2.0 V). The performance of these electrodes is compromised by a highly oxidizing surface above 4.3 V which results in a large irreversible capacity loss during the first cycle. Our attempts to pre-reduce the surface of the electrode particles with a mild reducing agent have indicated that it may be possible to increase the capacity and stability of these electrodes. A parallel investigation of highly lithiated Li_2MO_2 phases that form at 1.5-1.0 V has shown that their high reactivity in air compromises their possible use as “overdischarged” electrodes for offsetting the irreversible capacity loss that occurs at the negative electrodes of Li cells.

Progress that has been made in understanding and combating the solubility of LiMn_2O_4 spinel electrodes - a project that was initiated in the BATT program and transferred to the ATD program during FY2003 - will be reported.

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/polymer/gel and low-cost Li-ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized and characterized, both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2002: We have determined that layered manganese dioxides can be structurally stabilized, and that their electronic conductivity and cycling can be significantly enhanced by the addition of other transition metals. We will show the effectiveness of conductive coatings for enhancement of capacity. We will have completed an evaluation of LiFePO_4 as a base-case low cost cathode, and have shown that hydrothermal synthesis is not a viable approach. We will also have shown that vanadium oxides can also be stabilized by the addition of manganese ions to attain capacities greater than 200 mAh/g. In summary:

- LiFePO_4 : > 120 mAh/g for 100 cycles at 1 mA/cm².
- Layered $\text{Li}_x\text{Co}_z\text{Ni}_y\text{Mn}_{1-y-z}\text{O}_2$: 180-200 mAh/g for 5 cycles
- Layered $\text{A}_z\text{Mn}_{0.1}\text{V}_2\text{O}_5$ (A= NH_4 or TMA): ≥ 200 mAh/g for 6 cycles.

EXPECTED STATUS SEPT. 30, 2003: For low-cost Li-ion cells, we expect to identify the changes in stabilized LiMnO_2 structures as a function of current density and substitution level in $\text{Li}_x\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z\text{O}_2$, to determine the optimum substitution level and the role of cobalt, to determine the structure and composition of the vanadium stabilized LiMnO_2 and to increase its electrochemical capacity. For Li/polymer cells we expect to complete the evaluation of the manganese stabilized δ -vanadium oxides and to compare them to the iron phosphates. We will also have evaluated possible variants on iron phosphate as base case cathodes. Emphasis in all cases will be placed on understanding the reasons for capacity fade.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) To characterize the stabilized (geometrically and electronically) manganese oxide, determine the optimum substitution of Mn to obtain a capacity of 200 mAh/g, and to compare the best samples with iron phosphates. (b) To complete the characterization of manganese-stabilized vanadium oxides by June 2003 and to compare the best samples with lithium-iron and other phosphates for use in polymer or gel batteries.

****BATT Abstract:** see Task 2, Anodes Summary.

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.*, sol-gel, glycine-nitrate combustion). The microstructures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on low-cost, structurally stable materials such as manganese oxides and lithium iron phosphate, as well as novel materials with the potential for high energy density.

STATUS OCT. 1, 2002: Initial electrochemical characterization of sol-gel LiFePO_4 samples and O_2 layered manganese oxides will be complete. *In situ* XRD experiments on Li/tunnel MnO_2 cells will be underway.

EXPECTED STATUS SEPT. 30, 2003: Evaluation of Fe-substituted tunnel MnO_2 will be complete. Fundamental studies (*in situ* XRD analysis, diffusion coefficients, thermodynamic measurements, *etc.*) on unsubstituted tunnel MnO_2 will be complete.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:

(a) Go/no-go decision on sol-gel LiFePO_4 by April 2003.

(b) Analysis of *in situ* XRD results on Li/tunnel MnO_2 cells will be complete by September 2003.

Cathode Materials for the BATT Program

Marca M. Doeff
Lawrence Berkeley National Laboratory

Selected baseline cell chemistry cathodes and novel materials with the potential to meet USABC and FreedomCAR goals for energy density, power density, cost, and cycle life are synthesized and studied for this project. In FY2003, work was focused on LiFePO_4 and novel layered manganese oxides.

LiFePO_4

LiFePO_4 and doped variants were synthesized *via* a sol-gel method developed at LBNL, using a variety of processing conditions, and from iron acetate by a solid state method described in the literature. The electrochemical performance of these materials in Li cells was evaluated and correlated to mean primary particle size and residual carbon structure in the LiFePO_4 samples, as determined by Raman microprobe spectroscopy (R. Kostecki, F. McLarnon). For materials with mean primary particles sizes below 20 μm an association between structure and crystallinity of the residual carbon and improved utilization was observed. Addition of small amounts of organic compounds or polymers during processing results in carbon coatings with higher graphitization ratios and better electronic properties on the LiFePO_4 samples and improves cell performance in some cases, even though total carbon contents remain very low (<2%). These results suggest that it should be possible to design high power LiFePO_4 electrodes without unduly compromising energy density by optimizing the carbon coating on the particles.

Layered Manganese Oxides

Layered lithium manganese oxides with O2 structures may be prepared by ion-exchange of sodium-containing precursors with P2 layer arrangements. Several substituted O2 layered manganese oxides were synthesized and evaluated. These cathode materials do not convert to spinel upon cycling in Li cells, unlike O3 structures, but the electrochemical characteristics vary with substituents. An examination of the high capacity materials by XRD and NMR (E. Cairns, Y. Lee) indicates the presence of O3 as well as O2 phases. TEM and selected area electron diffraction experiments on $\text{Na}_{0.6}\text{Al}_{0.11}\text{Mn}_{0.89}\text{O}_2$ show that this material is an intergrowth of P2 and P3 phases, which changes to a stacking faulted O2/O3 Li analog upon exchange. In spite of the presence of O3 layers, no conversion to spinel was observed. This suggests it may be possible to prepare stable, high capacity layered manganese oxide electrodes by manipulating the amount and distribution of O2 and O3 phases in the intergrowths.

TASK STATUS REPORT

PI, INSTITUTION: J.B. Goodenough, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes - Novel Materials

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To evaluate alternative layered oxides as cathode materials for a Li-ion battery that operates between Ni(II) and Ni(IV).

APPROACH: Layered LiMO_2 oxides have been shown to exhibit a high Li^+ -ion mobility once a fraction of the Li is removed. On the other hand, these oxides are metastable and decompose upon removal of a large fraction of Li from between the host MO_2 layers. $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ contains Mn(IV) and removal of Li operates on the Ni(III)/Ni(II) and Ni(IV)/Ni(III) couples, both of which are pinned at the top of the $\text{O}^{2-}:\text{2p}^6$ band. Ohzuku and Mikimura have demonstrated a capacity over the range 2.5 to 4.3 V vs Li that approaches 150 m Ah/g for 30 charge/discharge cycles at room temperature. We have found that the capacity decreases sharply at higher current densities, which we suspect is the result of poor conductivity. We will investigate (1) whether we can increase the capacity at higher current densities by coating the particles with carbon and (2) the role, if any, of the Mn(IV) ions. Since small particle sizes are probably necessary, sol-gel synthetic routes will be employed.

STATUS OCT. 1, 2002: New project initiated 8/1/02.

EXPECTED STATUS SEPT. 30, 2003: $\text{Li}_2\text{NiMnO}_2$ samples with and without carbon will have been prepared and tested. Preliminary data will have been collected on other materials.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES: (a) Test the influence of carbon coating on layered and spinel Ni^{2+} , Mn^{4+} compounds operating on $\text{Ni}^{3+}/\text{Ni}^{2+}$ and $\text{Ni}^{4+}/\text{Ni}^{3+}$ couples and assess the role of Mn^{4+} in these compounds. September 30, 2003. (b) Investigation of Mn^{4+} ion by substitution of other M^{4+} ions. January 31, 2003.

Development of Advanced Cathodes $\text{LiMn}_x\text{Ni}_{1-x}\text{O}_2$ Revisited

Steen B. Schougaard and John B. Goodenough
Texas Materials Institute, University of Texas at Austin

In order to achieve a high voltage Li-ion rechargeable battery, it is necessary to use a transition-metal oxide in a high oxidation state as the cathode. The layered LiMO_2 oxides offer a high Li^+ -ion mobility for high-power applications. The commercial $\text{Li}_{1-x}\text{CoO}_2$ cathode contains expensive and relatively toxic cobalt. Moreover the capacity is limited by a solid-solution range $0 < x < 0.6$. In an attempt to replace cobalt by nickel and to increase the solid-solution range of Li in a $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ layered oxide, we are investigating samples with $\text{M}=\text{Mn}$ or Ti . The Ti is present as Ti^{4+} and the Mn is also expected to be present as Mn^{4+} . Moreover the $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox couples are pinned at the top of the $\text{O}^{2-}2p^6$ band, which should, in principle, allow oxidation of the Ni from Ni^{2+} to Ni^{4+} without a step in the voltage vs. discharge curve. A 4 V average voltage vs. Li/Li^+ at 0.1 mA/cm^2 has been reported (Ohzuku T, Makimura Y, *Chem Lett.* (8): 744) for $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with a capacity of $\sim 150 \text{ mAh/g}$, i.e., $0 < x < 0.5$. This would correspond to operation on the $\text{Ni}^{3+}/\text{Ni}^{2+}$ couple if Mn is present as Mn^{4+} . In an initial study of this system (Cushing BL, Goodenough JB, *Solid State Sciences*, **4**(11-12):1487), it was shown that coating the particles with carbon increased the performance at higher current densities, but careful examination of the XRD patterns showed that the capacity was limited by the presence of transition-metal ions in the Li layers.

Fully ordered phase-pure $\text{LiMn}_x\text{Ni}_{1-x}\text{O}_2$ has proven difficult to synthesize due to formation of Li_2MnO_3 and other unidentified impurity phases. Thus we have tried several synthetic strategies ranging from mechanical mixing of different transition metal precursors to sol-gel techniques. All of these have failed to yield fully ordered, phase-pure $\text{LiMn}_x\text{Ni}_{1-x}\text{O}_2$ when inspected by XRD. However, we present one technique that yields, reproducibly, a material that, by XRD, is well-ordered and phase pure. This technique is based on precipitation of mixed Ni/Mn oxalates in the presence of Li^+ , evaporation of the solvent, and decomposition at a relatively low temperature (375°C). Sintering can be performed at 1000°C in air without significant loss of Li. We present electrochemical data on two compositions from the $\text{LiMn}_x\text{Ni}_{1-x}\text{O}_2$ series ($x=0.5$ and $x=0.4$).

BATT TASK 5 DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: R. Kostecki and F. McLarnon, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVE: Establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity/power decline.

APPROACH: Our approach is to use Raman microscopy, scanning probe microscopy (SPM), ellipsometry, and standard electrochemical methods to characterize cell components taken from baseline BATT Program cells, fresh electrode materials, and thin-film model electrodes. Data to be collected include changes in electrode surface morphology and structure, electrode surface chemistry, and SEI thickness and composition, all of which accompany cell cycle-life tests.

STATUS OCT. 1, 2002: We defined relationships between electrode history, electrode surface properties, and temperature for baseline $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ cathodes. We completed our studies of structural disordering of graphite anodes during cycling at elevated temperatures and correlated the mechanism of SEI reformation upon cycling with graphite structural degradation.

EXPECTED STATUS SEPT. 30, 2003: We expect to develop good understanding of the key elements for good electrochemical performance of LiFePO_4 cathode, *i.e.*, identify the mechanism of electrode degradation in terms of changes of surface morphology and chemistry upon cycling and storage in BATT Program electrolytes. We will identify and confirm material limitations and specific degradation modes. We expect to determine and understand the effects of various synthesis routes, carbon coating, and impurities on the performance of LiFePO_4 cathodes. We will continue to investigate the effect of carbon disordering to determine its impact on long-term Li-ion cell performance. We expect to provide preliminary data from *in situ* Raman spectroscopy and current-sensing atomic force microscopy of individual particles of BATT baseline electrode materials. We plan to provide full diagnostic results for model thin-film LiMn_2O_4 cathodes.

RELEVANT USABC GOALS: 15 year life, < 20% capacity fade over a 10-year period.

MILESTONE: (a) Determine the effect of structure, morphology, carbon coating, and surface impurities on the electrochemical performance of LiFePO_4 electrodes - January 2003.

(b) Develop capabilities to carry out *in situ* Raman spectroscopy and current-sensing atomic force microscopy of individual particles of BATT baseline electrode materials - June 2003.

Spectroscopic and Microscopic Characterization of Electrode Surfaces

Robert Kostecki and Frank McLarnon
Lawrence Berkeley National Laboratory

We use Raman microscopy, current-sensing atomic force microscopy (CSAFM), and spectroscopic ellipsometry to detect, monitor and characterize surface phenomena, which occur in the components of baseline BATT Program cells, ATD Program cells, and thin-film electrodes in model cells. By combining these methods we can evaluate the surface and near-surface changes in electrode morphology, electrode surface chemistry, and SEI thickness and composition that may arise during cell cycling or storage at elevated temperatures. Our goal is to understand the mechanisms of surface phenomena and determine their impact on electrochemical performance life of Li-ion cells.

We have studied the role of elemental carbon additives with special emphasis on LiFePO_4 electrodes because of their intrinsically low electronic conductivity. We analyzed samples of raw LiFePO_4 powders, *i.e.*, before they were purposely mixed with carbon, that we obtained from BATT Program participants, and we concluded that all of them contain significant amounts of residual carbon (0.5-1.5% wt.). The structure of this residual carbon is highly amorphous because of the relatively low temperature of final heat treatment (600-700°C) typically used when LiFePO_4 is synthesized from organic precursors such as iron and lithium acetates or alkoxides. We also determined that the electronic conductivities of amorphous carbons produced by pyrolysis of organic precursors increases by 4 orders of magnitude for pyrolysis temperatures between 600 and 800°C.

We then analyzed LiFePO_4 raw powders in search of a correlation between residual carbon structure/conductivity and cathode electrochemical performance, in collaboration with Marca Doeff, BATT task 4.3, who provided raw samples of LiFePO_4 synthesized under different conditions and determined their electrochemical behavior. We concluded that the electrochemical behavior of LiFePO_4 is highly dependent upon the details of processing and that the physico-chemical properties of post-synthesis residual carbon determine the LiFePO_4 electrochemical performance. Further mixing of LiFePO_4 with carbon does not appear to have a significant effect on the electrode performance. We recommend the development of a synthesis route to produce a uniform and consistently “good” carbon coating on the LiFePO_4 based on an optimized final heat-treatment.

We completed our analysis of power fade mechanism of baseline BATT $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ cathodes at elevated temperatures. Based on our Raman microscopy data analysis and current-sensing AFM imaging results, we concluded that carbon recession and/or rearrangement unveils poor intergranular electronic contact within $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ agglomerates, which is responsible for the observed power and capacity loss. The mechanism of carbon additive retreat within the composite cathodes still requires better understanding and will be the subject of further work.

In situ and *ex situ* ellipsometric studies of the composite $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ cathodes revealed the presence of a thin 20-100 Å surface layer at the fresh cathode. Interestingly, the absorption coefficient of the electrode bulk and the surface film decreased significantly during aging. That observation is not only in concert with the carbon retreat process observed by Raman but also suggests reformation of the SEI layer at the cathode.

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen, Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: High-power Li-ion, high-energy Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge x-ray absorption spectroscopy. Exploratory work will be done on other techniques such as non-resonant inelastic x-ray scattering (NRIXS).

STATUS OCT. 1, 2002: We completed extensive *in situ* XRD on LiMn_2O_4 in the 4.1 V region. This included several new findings on the phase behavior and the effect of Li and O stoichiometry on electrode stability. The work also showed that electrolyte composition had major effects on the stability of LiMn_2O_4 at elevated temperatures. Work was also completed on the development of techniques for XAS studies of phosphorous decomposition products in cycled cells, and the techniques was applied to the ATD Program. Structural studies of new high-capacity cathodes and anodes will be ongoing. This includes XAS and XRD work on cathode materials such as LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. Anode work includes XRD on carbon-coated Si and Ge_3N_4 .

EXPECTED STATUS SEPT. 30, 2003: We expect to complete the XAS and XRD work on the cathode materials, LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. XRD on carbon-coated Si and Ge_3N_4 will also be completed. Exploratory work on non-resonant inelastic x-ray scattering NRIXS will be initiated. We expect to provide preliminary soft x-ray XAS data on various cathode materials, at the B, F, O, and P K edges and at the L_3 and L_2 edges of the transition metals.

RELEVANT USABC GOALS: 15-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) Complete *in situ* XAS and XRD studies of LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ by April 2003. (b) Complete *in situ* XAS and XRD studies of Si and nitride-based anode materials by June 2003.

Battery Materials: Structure and Characterization

James McBreen
Brookhaven National Laboratory

The primary objective is to develop and apply advanced diagnostic techniques, with sensitivity to bulk and surface processes, to monitor degradation processes in Li-ion batteries. These techniques are used to elucidate properties of starting materials that determine performance and stability of LiMn_2O_4 and other low cost cathode materials with higher capacity such as LiFePO_4 , $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

X-ray absorption spectroscopy (XAS) at the Fe K edge in both the transmission and electron yield does not support the uniform two phase moving boundary mechanism that has been proposed for the charge/discharge process in LiFePO_4 particles. Other possibilities are localized extraction/insertion of Li on the surface of LiFePO_4 particles or progressive nucleation of the charged/discharge phase.

In situ x-ray diffraction (XRD) and a combination of *in situ* and *ex situ* XAS was used to study the phase changes and the redox processes in $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. XAS was done at the K and $L_{2,3}$ edges of Ni, Co and Mn and at the O K edge. The results indicate that initially Ni exists as Ni(II) in $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ and Mn as Mn(IV). When Li is extracted during charge Ni(II) is oxidized to Ni(IV) and there is no change in the Mn oxidation state. In $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, Ni(II) is also oxidized to Ni(IV) during charge and Mn remains as Mn(IV). The Co exists as Co(III) in the initial material and its oxidation state does not change during charge. However the O K edge XAS indicates that charge compensation occurs on the O that is associated with Co.

Preliminary work was done on the development of a new technique for *in situ* studies of the O K edge in cathode materials. The technique is non-resonant inelastic x-ray scattering (NRIXS). It is sometimes referred to as x-ray Raman spectroscopy. Normally studies at the O K edge (543 eV) have to be done with soft x-rays under vacuum ($\sim 10^{-7}$ torr). With NRIXS we use hard x-rays (7 KeV) to get information at the O K edge. At this energy the x-rays can penetrate about 42 μ into a typical cathode material. This permits *in situ* studies of the O K edge.

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: High power Li-ion

BARRIER: Short battery lifetime

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use in-situ Fourier transform infrared (FTIR) spectroscopy to study the *interfacial chemistry* in model electrode/electrolyte systems to provide the basis to interpret more complex spectra recorded from ATD Program cell materials. For this year, we will add in-situ differential electrochemical mass spectrometry (DEMS) as a technique for studying *gas generation* from electrolyte decomposition reactions. These spectroscopies will be accompanied by classical electroanalytical methods such as cyclic voltammetry and the rotating ring-disk electrode (RRDE).

STATUS OCT. 1, 2002: Vinylene carbonate added (5 mol%) to PC-based electrolyte was found to prevent graphite exfoliation that normally occurs in PC-based electrolyte. The electrochemical oxidation of the saturated alkylcarbonate solvents used in Li-ion batteries occurs in dry (<20 ppm water) electrolytes only above 5 V. Water added to dry electrolyte causes the oxidation to occur at much lower potentials, e.g., <4 V.

EXPECTED STATUS SEPT. 30, 2003: Determine the oxidative and thermal stability of electrolytes with various electrode materials and impurities, e.g., water. Identify routes to improved stability *via* electrolyte additives and/or electrode pre-treatment.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: Identify at least one route to improved electrolyte stability *via* electrolyte additives and/or electrode pre-treatment.

High Power Li-Ion Battery

Philip Ross, Vera Zhuang, and Seung-Wan Song
Lawrence Berkeley National Laboratory

Both anodes and cathodes harvested from four BATT program pouch cells, PG 03, PG04, PG06 and PG13, were analyzed by ATR- FTIR. These cells exhibited substantially different levels of power fade/capacity loss from cycling under different conditions. It was thus hoped that we would see significantly different surface layers that could be correlated to the power fade/capacity loss. The components were “washed” by soaking in DMC for 24 hrs., followed by solvent evaporation in the glove box prior to spectroscopy analysis. The electrodes were then transferred from the glove box to the He-purged FTIR spectrometer sample chamber.

The FTIR spectra from cathodes from all four cells were essentially identical (the backgrounds were different due to differences in surface morphology). Most of the features could be readily assigned just to PVDF. Small features from a paraffinic compound could be traced (in independent experiments) to stripping of the polymeric corrosion inhibitor film on the Al current collector by the NMP (n-methyl pyrrolidinone) during solvent casting of the active layer, and subsequent deposition of the paraffinic residue upon drying. No evidence of a polyether or polycarbonate film was found. However, a more striking, and probably more important, result was related to the pre-existing carbonate in the cathode. FTIR analysis indicated the amount of carbonate in the virgin GEN2 cathode material is quite substantial, and decomposes simply upon soaking in LP40, presumably by reaction with the HF impurity. Presumably the carbonate is formed on the surface of active material by reaction with atmospheric CO₂.

The spectra obtained from anodes of four cycled pouch cells. These spectra were qualitatively similar, but quantitatively different. The overall spectra features from different cells could be fit with the same mixture of Li compounds. FTIR spectrum from PG04 anode in was simulated by superposition of individual spectra for lithium carbonate (Li₂CO₃), lithium succinate (LiO₂CCH₂CH₂CO₂Li), lithium oxalate (Li₂C₂O₄) and lithium methoxide (LiOCH₃). Succinate is a model compound for any number of carboxylates, *e.g.*, formate, acetate, propionate, *etc.*, that have the same strong features in the 1700 – 1550 cm⁻¹ from the –COOLi functional group. The vibrational features from of the PG13 anode clearly indicate that the passive film on the anode of the high temperature cycled cell PG13 (cycled at 60 °C) is quantitatively different from that in the cells cycled at lower temperature, *i.e.*, film is nearly purely inorganic carbonate. Since this cell had much higher power fade than the other cells, the absence of organic species, *e.g.*, methoxide, in the passive layer would appear to correlate with the power fade, *i.e.*, an organic component is needed to have sufficient Li ion conductivity. Carboxylates in the anode are shown to derive from electrochemical reduction of CO₂ evolving from the cathode during the formation cycles. Adventitious water present shifts the reduction path of alkyl carbonates from methoxide/oxalate (conductive) to carbonate/hydroxide/methanol (non-conductive).

Soft x-ray emission/absorption (XES/XAS) spectroscopy at the carbon and oxygen edges is being explored as a new diagnostic tool. Preliminary results will be presented.

TASK STATUS REPORT

PI, INSTITUTION: E.J. Cairns, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Synthesis and Characterization of Electrodes

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Rapid capacity fade

OBJECTIVES: The primary objectives are (1) to directly observe Li in BATT Program cathode materials, (2) characterize the Li atomic and electronic local environment, (3) determine changes in this environment with cycling, and (4) use this information to identify causes of capacity loss and propose improved electrode materials.

APPROACH: Our approach is to use ^7Li MAS-NMR to characterize BATT Program electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. XRD, magnetic susceptibility, and other data will also be used, as appropriate. NMR data on model failure mechanisms will be used to interpret the spectra. Structural information and information on the local Li environment will be gathered to improve our ability to design new electrode materials. This work will be carried out in collaboration with investigators who prepare and cycle electrode materials (*e.g.*, M. Doeff, K. Striebel, and others).

STATUS, OCT. 1, 2002: We obtained ^7Li MAS NMR spectra for several LiMPO_4 ($\text{M}=\text{Fe}, \text{Ni}, \text{Mn}, \text{Co}$) and $\text{Li}[\text{Mn}_x\text{Fe}_{1-x}]\text{PO}_4$ olivine compounds and established the hyperfine shift mechanism. This information will help elucidate the structural changes during electrochemical cycling. We identified the change in the Ni and Ni-containing environment as a significant mechanism of capacity fade in Gen2 electrodes. We identified the various local environments of Li in the layered $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$ materials and clarified the correlation between the local environments and electrochemical performance.

EXPECTED STATUS SEPT. 30, 2003: We anticipate that we will have completed an investigation of the capacity fade of several members of the family of layered $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$ materials. We will also complete our investigation of $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$ material in terms of the changes that occur during cycling, and the changes that accompany capacity loss and power loss. We will continue our investigations of the $\text{Li}(\text{Fe},\text{M})\text{PO}_4$ family of materials. As new materials are brought into the program, we will initiate NMR studies of these.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES: (a) Complete NMR investigation of layered $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$ materials by August 2003. (b) Complete investigation of the $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$ material in terms of changes that occur during cycling, and changes that accompany capacity and power loss by June 2003.

Cathode Material Studies Using NMR

Elton J. Cairns, Young-Joo Lee, and Jeffrey A Reimer
Lawrence Berkeley National Laboratory/University of California, Berkeley

Layered $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_{2.05}$: ^7Li MAS NMR spectroscopy has proven to be very useful in determining the local structure of $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_{2.05}$ layered compounds. Our new MAS probe and allows us to obtain higher resolution NMR spectra. Discrete resonances were observed depending on the metal substituents and these resonances were assigned to O2, O3, and T2-type environments. The compounds can be categorized into three classes. Al, Fe, Co, and Ni-substituted compounds contain both O2 and O3 type environments. Cu-doped material contains both O2 and T2 environments and Zn-doped material contains only O2 type environment. For all the materials, O2-type environment is the dominant phase. The compounds that contain both O2 and O3 type environments give higher initial capacity with the exception of the Fe-doped material. No Li cation substitution in the transition metal layer was observed. ^7Li NMR spectra were also obtained for $\text{Li}_y[\text{Al}_{0.11}\text{Mn}_{0.89}]\text{O}_{2.05}$ during and after electrochemical cycling. No change in the NMR spectrum was observed, indicating that there is no phase transition during the charging/discharging process. Even after 62 cycles, the spectrum does not show any clear evidence of new phase formation, suggesting that these materials are stable during deep cycling.

Olivine LiMPO_4 : ^7Li and ^{31}P NMR spectra were obtained for various LiMPO_4 compounds. A single ^7Li resonance of -92 to 57 ppm was observed depending on the transition metal. In contrast, a large ^{31}P hyperfine shift was seen, ranging from 1700 to 7300 ppm. The P NMR appears to be very informative in probing the local environment of the LiMPO_4 compounds, since the P atoms remain in the structure during the deintercalation process and ^{31}P NMR is more sensitive to the local environment than Li. ^7Li and ^{31}P NMR spectra were obtained for LiFePO_4 during the charging cycle. A single Li resonance without a significant change in the peak position was seen for all the states of charge, indicating that the Li cations remaining in the compound have the same local environment at all states of charge. This is consistent with the flat potential profile of this material. In contrast, an additional P resonance at higher shift than the original peak position was observed during the charging cycle. This high frequency resonance increases in intensity at the expense of the original resonance. The former was assigned to P in the FePO_4 phase and the latter to P in the LiFePO_4 phase. The presence of two ^{31}P resonances is consistent with the two-phase behavior of LiFePO_4 during cycling.

Gen2 $\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$: ^7Li NMR spectra of Gen2 cathode material show two dominant resonances at 0 ppm and 400 ppm, which can be assigned to Li with Co/Al-neighbors and to Li with Ni-neighbors, respectively. As charging proceeds, the resonance for the Li with Ni-neighbors gradually shifts to lower frequency and the linewidth becomes narrower. The signal for Li with Ni-neighbors decreases in intensity. The resonance for Li with Co/Al-neighbor increases in intensity at the beginning of charging (3.2 V- 4.0 V) and then decreases in intensity (4.2 V- 4.4 V). This suggests that the oxidation of Ni occurs during the entire charging range, whereas the oxidation of Co occurs only at high potentials (above 4.2 V). Some Gen2 electrodes that were treated following various protocols were also studied. An electrode with large capacity fading showed a significant decrease in intensity of the resonance due to Li with Ni-neighbors, suggesting that the capacity fading is mainly caused by the changes relating to the Ni-sites.

TASK STATUS REPORT

PI, INSTITUTION: G. Ceder, Massachusetts Institute of Technology
C. Grey, SUNY at Stony Brook

TASK TITLE - PROJECT:..Diagnostics - First-Principles Calculations and NMR Spectroscopy of Cathode Materials with Multiple Electron Transfers per Transition Metal:

SYSTEMS: Cation-doped lithium nickel manganese oxides

BARRIERS: High voltages, low electronic conductivity, stability, and limited electrochemical testing of cathode performance

OBJECTIVES: To engineer high-capacity, stable cathode materials by working with redox-active metal ions that can exchange multiple electrons in a narrow voltage range, focusing initially on the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple. Determine the effect of structure and cation doping on the Li deintercalation/ intercalation mechanisms and the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple.

APPROACH: Use solid-state NMR and XAS to characterize local structure and oxidation states as a function of state of charge and number of charge cycles. Use first-principles calculations (density functional theory) to identify redox-active metals, determine the relative stabilities of different structures and the effect of structure on cell voltages, and identify promising cathode materials for BATT Program applications. Use calculations and NMR to identify low-activation-energy pathways for cation migration and to investigate the effect of doping on conductivity.

STATUS OCT. 1, 2002: The analysis of the NMR data for $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ and $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$ during the first electrochemical cycle have been completed and compared with results from first-principles calculations. Investigation of multiple-cycled materials by NMR and calculations of the Li_2MnO_3 -NiO phase diagram are on going. Exploratory syntheses of Nb^{5+} -doped systems have been initiated.

EXPECTED STATUS SEPT. 30, 2003: NMR data for $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ $x = 1/2, 1/3, 1/10$ as a function of charging cycle will have been acquired and the analysis completed. XAS studies of the $x = 1/2$ and $1/3$ samples will be completed. A preliminary phase diagram for Li_2MnO_3 -NiO will have been calculated. Studies of cation doping (e.g., Nb^{5+} , Ti^{4+} , Co^{3+}) on local structure and cell potential will be ongoing. Applications of NMR and calculation methodology to other relevant systems under investigation by members of the BATT Program will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES: (a) Determine the site energies and voltages of the different Li environments in $(1-x) \text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2 \bullet x \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($M = 4+$) by first-principles calculations. Also determine the Li local environments and nickel oxidation state as a function of state of charge in $(1-x) \text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2 \bullet x \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($M = 4+$) by NMR spectroscopy and XAS. (Nov. 2002)
(b) Synthesis and preliminary characterization (powder diffraction and NMR) and electrochemical testing of the Nb^{5+} -doped materials. Perform initial calculations on the effect of cation doping (e.g., Nb^{5+}) on the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple. Perform (proton and Li) NMR studies of cation locations of iron phosphates and doped lithium (nickel) manganates in collaboration with S. Whittingham (SUNY Binghamton) and M. Thackeray (ANL). Complete XAS studies (with J. McBreen, BNL) of lithium nickel manganates. (May 2003)

First-Principles Calculations and NMR Spectroscopy of Cathode Materials with Multiple Electron Transfers per Transition Metal

Gerbrand Ceder, Massachusetts Institute of Technology, and Clare P. Grey, SUNY Stony Brook

Results from a detailed investigation of the structures of the cathode materials $\text{Li}[\text{Ni}_x\text{Mn}_{(2-x)/3}\text{Li}_{(1-2x)/3}]\text{O}_2$, with NMR and first principles calculations, will be described. The double redox couple $\text{Ni}^{2+}/\text{Ni}^{4+}$ in these materials makes them of interest as high capacity electrodes. Both methods indicate that the cations in the transition metal layer are not randomly distributed. Analysis of the ^6Li resonances assigned to Li in the Ni/Mn layers demonstrate that Li preferentially occupies sites near Mn^{4+} ions and avoids the Ni^{2+} ions, leading to configurations that are far from random. Calculations for $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ show that the Ni^{2+} and Mn^{4+} ions prefer to form alternating zig-zag rows. Although the disordering temperature is predicted to be near the synthesis temperature, stable ordered fragments are expected to persist at temperatures well above the order/disorder transition temperature, indicating that these materials will contain significant local order, even when quenched from high temperature. Such strong short range ordering will also lead to a significant dependence of structure on processing conditions. A model for cation ordering is proposed for the Li-excess materials (i.e., $x < 0.5$), which is based on the ordering found in the manganese $[\text{Li}_{1/3}\text{Mn}_{2/3}]$ layers of Li_2MnO_3 . Occupancies of 2:1 are obtained for Ni^{2+} substitution in the Li^+ and Mn^{4+} sites in the ordered $[\text{Li}_{1/3}\text{Mn}_{2/3}]$ layers, so as to maintain charge balance and to minimize the number of Li^+ ions in the Mn/Ni layers with Ni^{2+} cations in their 1st cation coordination sphere. Ni^{2+} ions in the Mn^{4+} sites tend to cluster, particularly in the samples containing higher Ni^{2+} contents, so as to produce regions with structures closer to those of $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$.

The NMR results clearly demonstrate that the Li is removed from both the Li layers and the transition metal (T.M.) layers on cycling. Calculations were performed in order to understand this phenomenon in more detail. Voltages for Li removal from different Li sites created by different ordering schemes were calculated, which showed that Li is removed from the Li and T.M. layers at similar potentials. The latter process is facilitated by Li vacancies in the T.M. layers. As the number of vacancies in the Li layers increase, the Li site in the T.M. layers becomes increasingly less stable, with respect to the adjacent tetrahedral site in the Li layers. Furthermore, at high concentrations of Li-ion vacancies, the activation energy for the octahedral to tetrahedral site migration is essentially zero. Thus, there is no kinetic barrier for this migration. The Li ions in the tetrahedral sites may then participate in the electrochemical process or remained pinned in the tetrahedral sites (depending on the local environments surrounding the sites). Li NMR showed that the Li ions return to the T.M. layers on discharging and that the process is reversible. Computations simulating the effect of overcharge indicate that the creation of Mn^{3+} may significantly reduce the stability of this material.

Investigations of the effect of cation doping (e.g., Co^{3+} , Ti^{4+} , Nb^{5+}) and multiple charge cycles on local structure are underway. Long term cycling of $\text{Li}[\text{Ni}_x\text{Mn}_{(2-x)/3}\text{Li}_{(1-2x)/3}]\text{O}_2$, shows some changes in the local structure, as probed by Li-NMR. These Li NMR studies were also complemented by ^2H and ^1H NMR studies of these materials (with P. Bruce, St. Andrews), to explore the role that decomposition of the electrolyte plays in the long-term stability of these materials. Results for the Co-doped systems indicate that the Co, Mn and Ni ions are intimately mixed at a local level. These samples also contain some Li in the T.M. layers. Interactions with other BATT members will be described. These include XAS and powder diffraction studies with J. McBreen (BNL; $\text{Li}[\text{Ni}_x\text{Mn}_{(2-x)/3}\text{Li}_{(1-2x)/3}]\text{O}_2$ and Co^{3+} -doped materials) and NMR characterization of the cathode materials synthesized by M. Thackeray (ANL; doped $\text{Li}[\text{Ni}_x\text{Mn}_{(2-x)/3}\text{Li}_{(1-2x)/3}]\text{O}_2$) and S. Whittingham (SUNY Binghamton; iron phosphates).

TASK STATUS REPORT

PI, INSTITUTION: J. Evans and T. Devine, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Corrosion of Current Collectors

SYSTEMS: Low-cost Li-ion

BARRIER: Uncertain and possibly inadequate corrosion resistance of Al current collectors

OBJECTIVES: Characterize the long-term corrosion performance of Al current collectors in Gen 2 chemistry baseline cells. Determine the mechanism of passivation in Gen 2 electrolyte and identify the passive film responsible for the corrosion resistance of Al current collectors in Gen 2 cells. Identify electrolytes of multi-component salts that are optimized for battery service and that are noncorrosive to Al current collectors.

APPROACH: Inspect for corrosion damage the Al current collectors taken from the many tens or hundreds of batteries that have been life-tested following a well-defined testing protocol. ATD Program cells are the most likely source of data. Analyze by Extreme Value Statistics the results of the failure analyses and predict 10-yr and 15-yr performance of Al current collectors in Li-ion batteries. Use a combination of electrochemical tests (anodic and cathodic polarization and concurrent measurement of mass change using electrochemical quartz crystal microbalance; electrochemical impedance spectroscopy) and surface analytical techniques (optical and scanning electron microscopy, energy dispersive x-ray analyses and Raman spectroscopy) to investigate the mechanism of corrosion and passivation of Al in baseline electrolyte and in other electrolytes relevant to Li-ion batteries (*i.e.*, electrolytes of multi-component salts that are noncorrosive and are optimized for battery service).

STATUS OCT. 1, 2002: Life-tested batteries that are to be autopsied for corrosion-related damage of current collectors have been identified and grouped according to the identities of the electrolytes, cathode materials, and testing protocol. Inspection of the current collectors from life-tested batteries has begun. Preliminary electrochemical experiments to investigate passive film formation on Al in Gen 2 electrolyte has been completed.

EXPECTED STATUS SEPT. 30, 2003: Characterization of the performance of Al current collectors in life-tested batteries will be complete. The 10-yr and 15-yr performances of Al current collectors in Gen 2 electrolyte will be calculated using Extreme Value Statistical Analyses. The accuracy of the predictions will be a function of the quantity and quality of the data acquired from the failure analyses. The mechanism of Al passivation in Gen 2 electrolyte will be determined. The mechanism of Al passivation in electrolytes of multi-component, non-corrosive salts will be well underway.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade.

MILESTONES:

- (a) 10-year and 15-year performance of Al current collectors in Gen 2 batteries will be predicted based on Extreme Value Statistical Analyses of life-tested cells by August 2003.
- (b) Mechanism of Al passivation in Gen 2 electrolyte will be determined by August 2003.

Corrosion of Aluminum Current Collectors in Lithium Ion Batteries

Xueyuan Zhang, James W. Evans and Thomas M. Devine
Lawrence Berkeley National Laboratory/University of California, Berkeley

Our research is focused on three topics related to the corrosion behavior of Al current collectors in Li-ion batteries. First, we are investigating the passive film that forms on Al in the Gen 2 electrolyte. Surface enhanced Raman spectroscopy (SERS) is used to obtain the *in situ* vibrational spectrum of the surface film that forms on Al in Gen 2. The Raman spectra were obtained as a function of applied potential and the spectra serve as fingerprints for identifying the species present on the surface of the Al.

The electrochemical behavior of Al in Gen 2 was characterized by a combination of potentiodynamic anodic polarization and electrochemical impedance spectroscopy. During the polarization experiments, the anodic current and mass change of the Al electrode are simultaneously measured as a function of applied potential. The change in mass of the Al was measured with the aid of an electrochemical quartz crystal microbalance. Collectively, the polarization measurements, SERS, and impedance spectra provide information to identify the surface film that forms on Al in Gen 2.

Second, we are investigating the localized corrosion resistance of Al in Gen 2. Aluminum current collectors exhibit very good resistance to uniform corrosion in Gen 2. If the Al current collectors were to fail by corrosion, a likely failure mechanism is crevice corrosion. For example, Al might suffer high rates of localized corrosion in regions where a small gap develops between the Al and the cathode. We are characterizing the crevice corrosion resistance of Al in Gen 2 by determining the critical crevice corrosion temperature (CCCT). The CCCT is the minimum temperature at which crevice corrosion occurs in a creviced sample that is anodically polarized to a particular potential.

Third, we are determining the practical importance of corrosion of Al in commercial and laboratory batteries. Specifically, we have microscopically examined the surfaces of Al current collectors that were removed from used commercial batteries and life-tested laboratory batteries obtained from Marca Doeff and Kathy Striebel. We have observed corrosion of Al current collectors and the corrosion localized, rather than uniform.

BATT TASK 6 MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Side reactions, dendrite formation, low capacity, safety

OBJECTIVES: Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Develop model of dendrite formation on Li metal. Use simulations to improve understanding of the SEI layer. Use simulations to understand performance limitations of baseline BATT chemistries and to identify promising design options.

STATUS OCT. 1, 2002: Analysis of the effect of side reactions on measurements of transport properties is completed. Molecular-dynamics simulations of diffusion coefficients in multicomponent electrolytes such as LiPF_6 in EC:DMC will be nearing completion. Diagnostic experiments of the SEI layer on lithium-tin electrodes are completed. Modeling of dendrite growth and initiation will be ongoing. Modeling of the SEI layer will be ongoing. Modeling the performance of baseline BATT chemistries LiFePO_4 and $\text{Li}_{0.4}\text{MnO}_2$ will be in progress. A preliminary model to describe the concentration and voltage profiles in polymer laminates will be completed.

EXPECTED STATUS SEPT. 30, 2003: Molecular dynamics simulations of diffusion coefficients will be completed. Modeling dendrite initiation in viscous and elastic electrolytes will be ongoing. Comparison of SEI simulations with experimental results and refinement of the model will be ongoing. Modeling of the performance limitations of LiFePO_4 will be completed, and modeling of other BATT baseline chemistries will be ongoing. Simulation of the behavior of conductive polymers for overcharge protection will be completed. The model for the behavior of polymer laminates will be completed and compared to experimental data.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES:

1. Develop model of electronically conducting polymers for overcharge protection by May 1, 2003.
2. Model of LiFePO_4 and determination of performance limitations by August 1, 2003.

Improved Electrochemical Models

John Newman

Lawrence Berkeley National Laboratory/University of California, Berkeley

Research in Tom Richardson's group has shown that electroactive polymers (*e.g.*, polythiophene) mixed into the separator can protect cells against overcharge by becoming electronically conductive under high oxidizing potentials. A model has been developed to understand how the short works. Essentially, the cell is transformed from a battery into a resistor whose resistivity varies with position across the separator. The resistor is then transformed back into a battery after the charging current is turned off. The simulations show that the polymer's degree of oxidation varies across the separator, being more oxidized (and thus more conducting) closer to the positive electrode, and confined to the neutral (insulating) state in a submicrometer-thick region adjacent to the negative electrode. The result is that the cell voltage is constant during overcharge, and this voltage depends *only* on the properties of the polymer short and is independent of the positive electrode chemistry. The model matches experimentally observed trends of the effects of polymer conductivity and current density. The model has helped us identify which parameters control the behavior of the short, to allow rational design and selection of materials.

A model has been developed to predict the behavior of the natural graphite/LiPF₆/iron phosphate baseline chemistry. While the graphite electrode model has previously been developed in the group, a model for the phase change and diffusion in iron phosphate was completed using a shrinking-core approach. Experiments were performed to extract the equilibrium potential of the iron phosphate electrode and used with the model to predict discharge curves at various rates in a half-cell configuration. Comparison to experiments shows excellent fits. Simulations show that ohmic drops in the matrix phase and diffusion resistances within the iron phosphate particles limit the cell performance. Subsequently, half-cell experiments on the graphite electrode, taken from Kathy Streibel's group, were compared to the mathematical model. These two half-cells models were then combined to predict the behavior of the baseline. Simulations suggest that while the present cell design shows performance (80 Wh/kg) far below the DOE specific energy goals (150 Wh/kg), significant improvements can be achieved by changing the balancing of the cell and increasing the electrode thickness.

In ongoing work, a model was developed to study the behavior of the SEI layer on the negative electrode. Preliminary results suggest that the rate of film growth increases with Li content and that the irreversible capacity loss due to film formation is small. We propose to explore this model further to understand the implications of this layer on the observed power fade in cells.

In order to address the problem of dendrite growth in Li-polymer cells, a theory has been developed to correlate surface roughness to measurable mechanical properties. This theory extends those previously developed in the literature to include properties like the elastic modulus and viscosity, in addition to the surface tension. We will use this theoretical framework to identify conditions, if any, under which dendrite initiation can be inhibited.

Finally, we propose to use a model-based approach to compare and optimize the capabilities of the various baselines chemistries.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan

TASK TITLE - PROJECT: Modeling and Experimentation – Electrochemical Materials

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: Predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Use simulations to design combinations of conductive additives to improve battery performance, and specifically reduce irreversible capacity losses (ICL). Perform complete studies of electrode (both anode and cathode) conduction, with cell testing to confirm the materials' effect on battery performance. Show improvement in performance of baseline materials with strategic additives, as determined by simulation.

STATUS OCT. 1, 2002: Confirm structure/function relationships in carbon additives in baseline systems. Determine effect of lamination on contact resistance in baseline systems. Determine initial relationship between ICL and conductivity of anode. Initiate testing of cathodes. Initiate simulations of cathode conductivity.

EXPECTED STATUS SEPT. 30, 2003: Experiments (LBNL and UM) and simulations on conduction in baseline anodes and cathodes, with correlations developed relating material composition and cell capacity losses will be completed. Modeling of other BATT Program baseline chemistries will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES: (a) Determine relationship of ICL to electrode conductivities by May 2003.
(b) Carry out simulations of conduction in cathodes with experimental verification by June 2003.

Improved Conduction Models: Anodes And Cathodes

Ann Marie Sastry
University of Michigan

Resistivity was examined in anodes and cathodes, experimentally and through simulations, in close collaboration with other BATT researchers (Striebel, Zaghbi). The effect of carbon particle coating with amorphous graphite on conductivity was examined. Also, pressing of anodes, and its effect on conductivity and irreversible capacity loss (ICL) in cells tested at LBNL was studied.

In order to generate simulation data, we also performed extensive image analysis on as-received anodes and cathodes from LBNL. Data on particle size and shape was used to predict electrical resistance in the active layers of electrodes, and contact resistance between layers. Conduction experiments were performed and analyzed using a protocol and closed-form theoretical approach developed in the last project year. We found that the coating shape has a significant effect on conduction, both experimentally and through our simulations, and that simulations were able to quite satisfactorily predict top-layer resistance in anodes. Also, we investigated use of 3D models in this project year, and found that 3D packing effects play a significant role in all of the relevant program electrochemistries, due to the size of particles presently used for conduction, relative to electrode thickness. Pressing of electrodes resulted in improved conductivity, and the close match with simulations verifies that these simulations can be used by other teams to design electrodes for conductivity.

Testing of cathodes resulted in generation of data sent to LBNL (Newman) for use in electrochemical simulations. Because of the low overall conductivity in cathodes, the experimental uncertainty in conductivity is higher than in anodes, thus, use of bounding parameters, especially for contact resistance, was suggested.

Results on conductivities suggest that volume fractions of conductive additives (carbons) can be maintained for thicker electrodes required for DOE specific energy goals with predictable, stable conductivities. Also, simulations indicate that the coating of particles is penetrable, based on resulting conductivities. Finally, volume fractions of conductive additives can be significantly reduced, in all probability, using higher-aspect ratio particles, thus reducing electrode mass. We propose study of these materials in collaboration with Striebel's group.

PROPOSALS UNDER REVIEW

ORGANIZATION <i>(Principal Investigator)</i>	TITLE	STATUS
Hydro-Québec <i>(K. Zaghib)</i>	Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials	Renewal Proposal - Contract Placed
University of Texas at Austin <i>(J.B. Goodenough)</i>	Cathodes - Novel Materials	Renewal Proposal - Contract Placed
Massachusetts Inst. of Tech. <i>(G. Ceder)</i> SUNY @ Stony Brook <i>(C. Grey)</i>	High Capacity, Stable Cathode Materials in Lithium and Lithium-Ion Batteries An Investigation of the Stability of the Lithium Metal Interface	Renewal Proposal - In Negotiation
University of Michigan <i>(G.A. Nazri, D. Curtis)</i>	Novel Composite Anodes for Lithium-Ion Batteries - Preparation, Performance, and Safety Aspects	Renewal Proposal - Contract Placed
SUNY Binghamton <i>(M.S. Whittingham)</i>	Novel Anode Materials and Novel Cathode Materials	Renewal Proposal - Contract Placed

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)
QUARTERLY REPORT FOR JANUARY – MARCH 2003
CALENDAR OF UPCOMING EVENTS

April 2003

27 - May 2 203rd Electrochemical Society Meeting – Paris France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

June 2003

1 - 6 1st International Conference on Polymer Batteries and Fuel Cells (PBFC-1) – Jeju Island, Korea (Conference Headquarters Office, Department of Chemical and Biomolecular Engineering, KAIST, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, KOREA; 82-42-869-3925; fax: 82-42-869-3910; pbfc@pbfc.kaist.ac.kr; <http://pbfc.kaist.ac.kr>)

22 - 27 14th International Solid State Ionics Meeting - Monterey, CA (Turgut Gur, Stanford University, turgut@stanford.edu; <http://www.ssi-14.net/>), Asilomar

August 2003

31 – Sept. 5 54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

September 2003

17 – 20 High Energy Density Electrochemical Power Sources – Nice, France (Marcelle Gaune-Escard, HEDEPTS 2003, Polytech'Marseille, IUSTI, 5 rue Enrico Fermi, 13453 Marseille cedex 13, France; 33 4 91 10 68 82; fax: 33 4 91 11 74 39; email: battery@polytech.univ-mrs.fr; <http://iusti.univ-mrs.fr/HEDES2003/index/html>)

October 2003

12 - 17 204th Electrochemical Society Meeting – Orlando, FL (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

May 2004

9 - 14 205th Electrochemical Society Meeting – San Antonio, TX (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

September 2004

55th ISE – Thessaloniki, Greece (Prof. E. Theodoridou)

October 2004

3 - 8 206th Electrochemical Society Meeting – Honolulu, HI (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)